CANADIAN
JOURNAL OF RESEARCH

CONTENTS

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Notice to Contributors

THERMAL CONDUCTIVITY OF INSULATING MATERIALS[1]

BY E. A. ALLCUT[2] AND F. G. EWENS[3]

Abstract

The physical significance of "thermal conductivity" is well known, but this term has been applied commercially to a combination of conduction, convection, and radiation, which combination may vary considerably in a single material. Experimental evidence is advanced to indicate the undesirability of using this method of comparing the relative usefulness of different insulating materials.

Most of the thermal insulating materials sold in Canada and in other countries are compared on the basis of their thermal conductivities or k factors. Fourier's law is usually expressed in the form:

$$Q = kA \frac{dt}{dx},$$

where Q is the heat transmitted per hour,

A is the area perpendicular to the heat path,

$\frac{dt}{dx}$ is the temperature gradient,

k is the coefficient of conductivity.

If this basis of comparison is to be valid, the value of k must be constant for a definite material at a specified density. This then, is the physical concept of "conductivity", but the results obtained in practice, using the hot plate method of testing, are also affected by the following factors, which themselves are liable to vary:

(a) Surface resistances to the transfer of heat,

(b) The effects of convection currents (and in some cases also radiation effects).

The authors have found, in a large number of tests, that size, thickness, and density all have an influence on the "conductivity" which is obtained by calculation from the "conductance" or "resistance" measured by means of hot plate tests (1). In such instances, the "conductivity" of commerce is very different from the conductivity of Fourier's law, and the former term

---

[1] *Manuscript received July 3, 1939.*

Contribution from the Department of Mechanical Engineering, University of Toronto, Toronto, Canada.

[2] *Professor, Department of Mechanical Engineering, University of Toronto.*

[3] *Instructor, Department of Mechanical Engineering, University of Toronto.*

should be either dropped entirely or replaced by another. The authors do not see any reason why the word "conductivity" should be retained for the property (conductance × thickness), as all calculations of heat losses from buildings, etc., must be made by using the "conductance" or "resistance". Why interpose an additional property which is unnecessary and may be very misleading?

Surface Resistance

Some years ago (1) the authors investigated the effects of varying thicknesses of material on the "conductivities" of various materials and suggested that the rising values of k with increasing thickness were probably due to increased resistance to the transmission of heat through the surface layers, particularly in the case of fibreboards and other similar materials. This question was further investigated by Babbitt (3) who found that the surface resistance of fibreboards was negligible when the outer layers were removed by sanding for the purpose of varying the thickness. One of the specimens, however, gave a value of k that increased from 0.409 to 0.429 when the thickness of the board was reduced from 2.081 to 1.495 in., by removing the surface layer. This difference is probably due, as he suggests, to the fact that the surface layers are arranged differently from those in the interior of the board. This matter has been studied recently at the University of Toronto, where
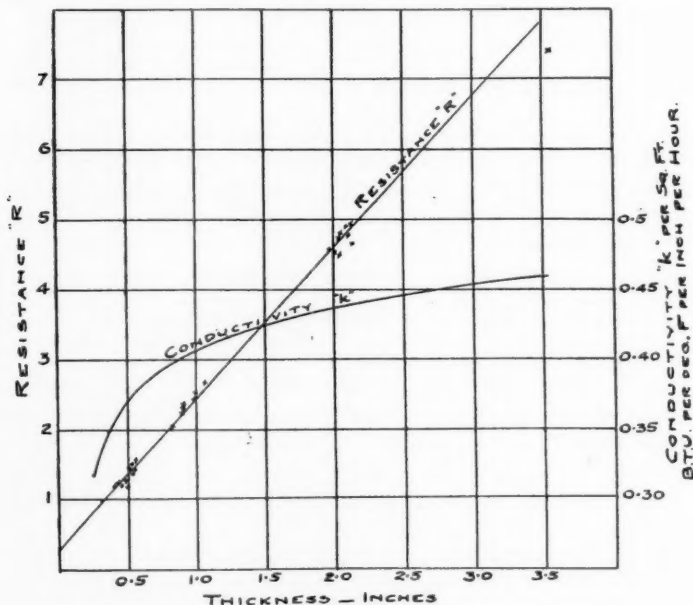
FIG. 1. *Conductivity, resistance, and thickness of fibreboards.*
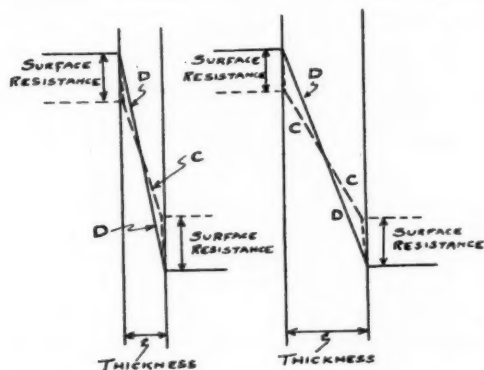
FIG. 2.   *Influence of thickness on apparent temperature gradient.*

structures were examined microscopically by Dr. D. H. Hamly (Fig. 8) and where air infiltration tests (2) revealed the fact that the ease with which air passes through fibreboards is practically independent of their thickness, being a function of the density.   This indicates the predominant influence of the surface layers on porosity, and by inference, their probable importance also in heat transfer.   Fig. 1 shows a mean curve drawn through a number of test points obtained with fibreboards of different makes and thicknesses.   On the assumption that the curve of resistance against thickness is a straight line (3), the residual resistance at zero thickness is an indication of the amount of superficial resistance, and the influence of this on the calculated value of k is indicated in Fig. 1.   The true conductivity of the material is indicated by the slope of Curve C, Fig. 2, while that obtained by the hot plate test is given by Curve D.   The former probably remains constant, while the slope of the latter varies with different thicknesses, so that in Fig. 1 the value of k rises from 0.37 for a 0.5 in. thickness to 0.44 for 2 in.
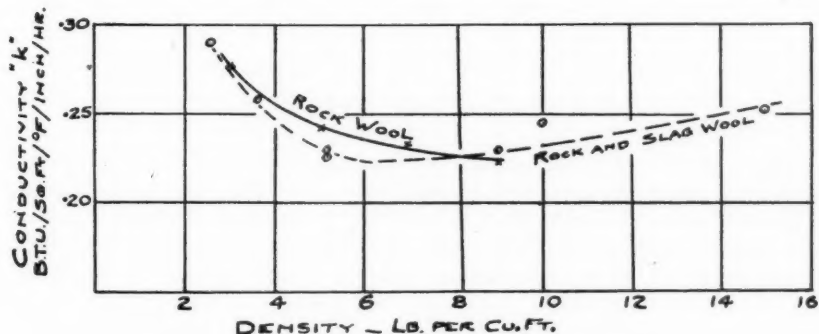
FIG. 3.   *Values of k for fibrous materials at various densities.*
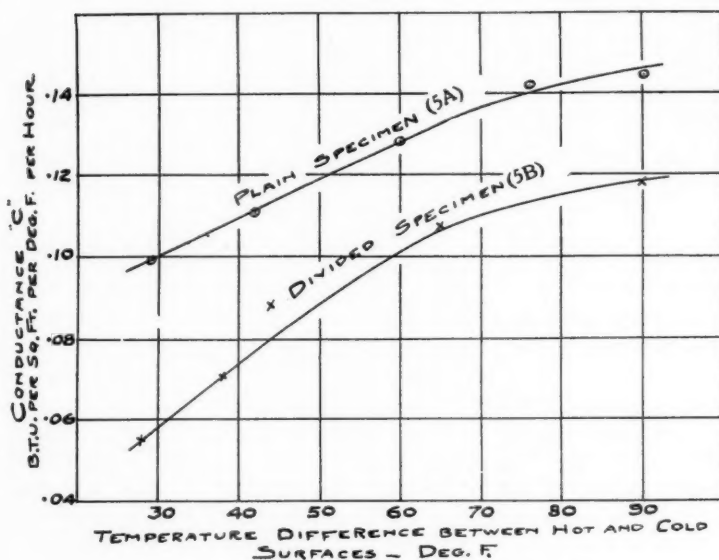
FIG. 4.   *Conductances of plain and divided specimens.*

Convection Effects

Characteristic curves showing the effects of density on the "conductivity" of packed fibrous materials are shown on Fig. 3* and these indicate that some factor other than conduction is affecting the heat transfer even when packing densities as high as 9 lb. per cu. ft. are used.   The smaller air spaces and the greater number of contacts between fibres at high densities tend to increase the heat transmitted by conduction, and yet the experimental curves show decreases in heat transmission up to certain optimum densities.   It is probable, therefore, that even at these high densities, some of the heat is transmitted by convection.   Similar indications are also obtained when tests are made on
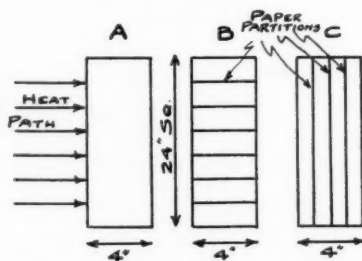
FIG. 5.   *Form of specimens referred to in Figs. 4 and 6.*

* *See also curves in "Mechanism of Heat Flow in Fibrous Materials" (4).*

subdivided specimens.   Fig. 4 gives results obtained in tests made on rock wool packed to a density of 10 lb. per cu. ft., using alternately a plain specimen (Fig. 5, A) and one divided into a number of horizontal layers (Fig. 5, B). Further tests have recently been made with a different material (density, 8 lb. per cu. ft.) tested as in Fig. 5, A, and also with vertical paper partitions as shown in Fig. 5, C.

The first tests were made on the specimen shown in Fig. 5, C, with thermo-couples placed against the surfaces of the paper partitions, and the value of k calculated from the readings taken on a guarded hot plate was 0.342 B.t.u. per sq. ft. per in. thickness per degree (F) temperature difference per hr. The temperature gradient obtained from the readings after steady conditions were obtained is given in Fig. 6.   The paper partitions were then removed
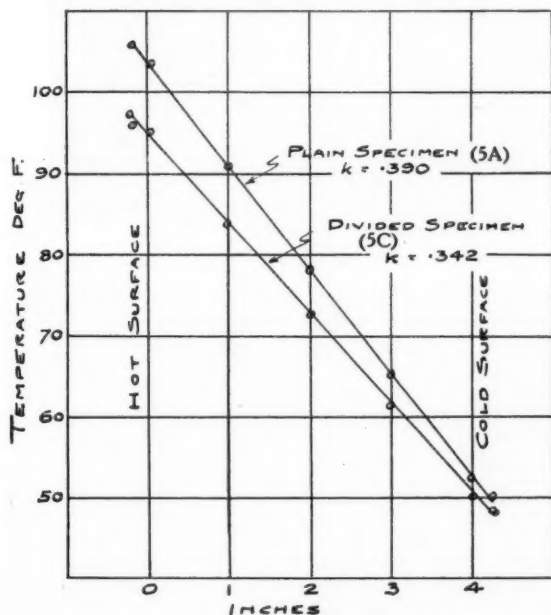
FIG. 6.   *Temperature gradients through slag wool.*

and the test was repeated with the same specimen and with the thermocouples similarly spaced, the value of k for the same heat input being 0.385.   As the mean temperature and temperature difference were both lower than those in the previous test, the heat input was increased to give a greater temperature gradient, as indicated by the curve for "plain specimen" in Fig. 6, whereupon the calculated value of k increased to 0.390.

Previous tests (1) had shown that the temperature difference employed between the hot and cold sides of the specimen had an influence on the cal-

SURFACE

CUT EDGE
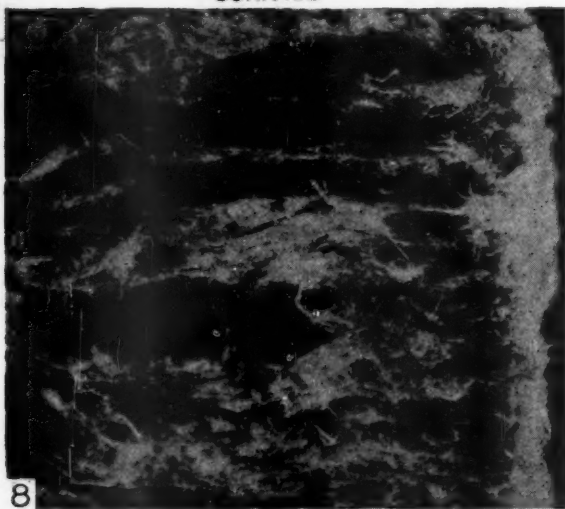
SURFACE

Fig. 7.   Enlarged photograph of Shredded Redwood Bark.

Fig. 8   Structure of fibreboard.

culated values of k for thick specimens, but that this effect was small with thin specimens.

A number of tests were made on Shredded Redwood Bark (a commercial insulating product), packed to a density of 5 lb. per cu. ft., the same temperature difference and mean temperature being maintained in each case. The values of k for thicknesses of 1, 2, 3, 4 in. are given in Table I.

TABLE I

CONDUCTIVITIES *(k)* OF SHREDDED REDWOOD BARK AT VARIOUS TEMPERATURE DIFFERENCES
AND THICKNESSES, AS OBTAINED ON HOT PLATE APPARATUS, 24 IN. SQUARE

DENSITY OF MATERIAL, 5 LB. PER CU. FT.; MEAN TEMPERATURE, 90° F.

Temperature difference across specimen, °F.	10	20	40	60	80	100
k for 1 in. thickness	0.300	0.330	0.370	0.390	0.395	0.400
k for 2 in. thickness	.300	.340	.395	.425	.450	.460
k for 3 in. thickness	.300	.345	.410	.455	.490	.510
k for 4 in. thickness	.300	.350	.420	.480	.525	.550

The above values of k are in B.t.u. per square foot per inch thickness per degree F. temperature difference per hour.

These differences are difficult to account for unless it is assumed that convection currents exist in the packed material, and that they may be reduced either by increasing the density of the material, or by dividing the specimen into smaller cells.

Conclusion

The evidence given above indicates that, in the case of fibrous insulating materials, the property calculated from the "conductance" obtained by hot plate tests is not conductivity, but is a combination of various properties depending largely on the size, structure, and density of the specimen tested, and therefore its continued use in practice is undesirable.

An enlarged photograph of the structure of Shredded Redwood Bark is shown in Fig. 7. It seems unreasonable to apply the term "conductivity" to the transmission of heat through structures of this kind.

References

1. ALLCUT, E. A. and EWENS, F. G.   School of Engineering Research, University of Toronto, Bull. 149.   1937.
2. ALLCUT, E. A.   School of Engineering Research, University of Toronto, Bull. 158.   1939.
3. BABBITT, J. D.   Can. J. Research, A, 16 : 82-87.   1938.
4. FINCK, J. L.   Bureau of Standards, Research Paper No. 243.   1930.

DESCRIPTION OF A PRESSURE CELL FOR THE MEASUREMENT OF EARTH PRESSURE[1]

By I. F. Morrison[2] and W. E. Cornish[3]

Abstract

The vibrating wire method for measuring strains is used to determine the pressure applied to an earth pressure cell. The construction of the cell, the principle on which it acts, and electrical circuits are described.

Introduction

Although much has been written on the theory of earth pressures on retaining walls and below foundations, the present need is of measurements to confirm the theory and to establish such basic principles as may lead to a practical method for the computation of such earth pressures. A number of earth pressure measuring cells have been developed, but they fall short, somewhat, of what is hoped will be the ultimate development of such apparatus. It is not the purpose of this paper to give a critique of previous attempts but rather to describe still another attempt to develop a suitable earth pressure cell.

The requirement of a suitable earth pressure cell is that it shall be capable of measuring with requisite accuracy the active earth pressure that comes upon it. Some pressure cells already in use do not meet this requirement. In addition, the cell must be "hard", *i.e.*, it must measure the pressure with as little movement of the surface, to which the external pressure is applied, as possible. Moreover, the measurements must be recorded on instruments at some distance from the cell itself and, therefore, by indirect observation. In addition, it must be reliable over a considerable time interval.

To meet these requirements, it was decided to use the vibrating wire method, and to this end preliminary studies were made of the electrical arrangement to determine the most suitable size and limitations of length of wire and the best position of the electromagnets for driving the wire and picking up its vibration. This successfully accomplished, the cell was designed with due regard to the hardness requirement and its practical and rugged construction. Its range was planned to extend to an equivalent soil pressure of 7500 lb. per sq. ft., which required a load of slightly over 1000 lb. on the cell.

Description of Cell

The working part of the cell consists of a stiff, T-shaped beam which rests on a properly located knife-edge fulcrum. At the free ends of the beam, short arms project downwards. The wire is securely held at its ends by these

arms. It passes, below the beam, through a slot in the fulcrum. The T-shape was adopted in order to secure a three-point support for the cover plate through which the soil pressure is transmitted to the beam and thereby to eliminate the effect of flexural strain of the cover plate on the readings given by the electrical equipment.

In addition, since any cell for such purpose must be capable of continued operation over a long period, it was decided to lessen the possibility of creep in the wire tension by working from a higher tension to a lower, and for that purpose the single fulcrum was adopted. Besides, the single fulcrum fairly well eliminates the effect of distortion of the base of the cell. Fig. 1 shows the arrangement as described above and also the arrangement of the magnets in the vicinity of the tight wire.

PLAN, COVER PLATE REMOVED

SECTION

FIG. 1
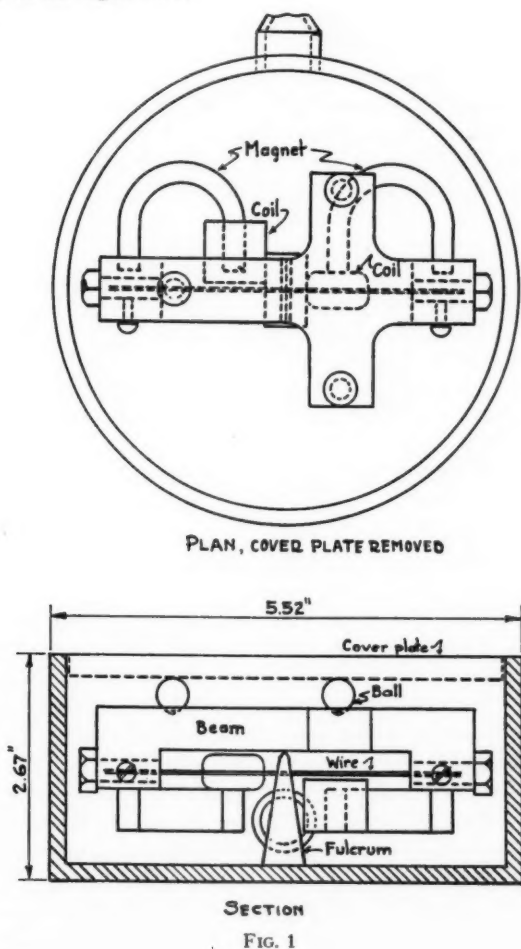
The T-beam was cut from a steel plate $\frac{1}{2}$ in. thick and, as the point of application of one-third of the total pressure on the cover plate is but $1\frac{1}{4}$ in. from the fulcrum, the beam is quite stiff. For full load the computed movement of the cover plate amounted to about 0.001 in., so that the cell may be considered fairly "hard".

From previous experimental work, the most suitable size of wire was found to be 0.020 in. diameter and a piece of steel piano wire, as near this size as practical, was used. The clear length of the wire is about $2\frac{3}{4}$ in. and the ends are securely fastened into steel sockets which pass through the arms at the ends of the beam. The sockets are threaded and provided with nuts for tightening the wire to its initial tension. Also set screws are provided to keep the sockets from turning.

Electrical Set-up

As previously mentioned, the vibrating wire method is used to measure the pressure on the cell. This method consists of causing the wire to vibrate and measuring the frequency of vibration of the wire. As load is applied, the tension in the wire decreases; this decreases the frequency and thus gives a measure of the pressure on the cell.
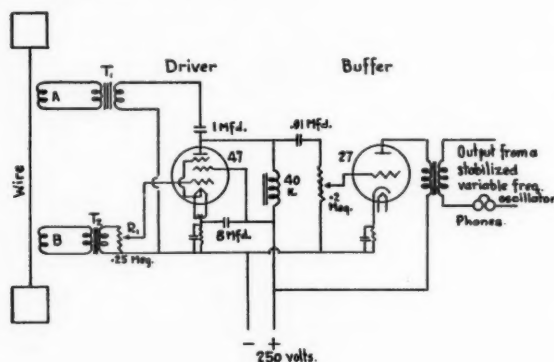
FIG. 2

In Fig. 2, *A* and *B* are the coils from a telephone headset. As shown in Fig. 1, these coils are mounted on the magnets from the headset and these magnets are fixed to the arms which hold the ends of the wire. Thus, there is a magnetic flux passing through each coil, across the gap between the coil and the wire, and along the wire back to the arm. Coils *A* and *B* are mounted at right angles so as to prevent mutual coupling between them. The impedances of the coils are matched to the impedances of the driver tube by using suitable transformers T_1 and T_2. A variable resistance R_1 is used to control the amplitude of vibration of the wire. The driver tube is a power amplifier pentode, No. 47. The reason for using this tube is its high amplification factor.

The operation of the driver is as follows: Coil A, the driving coil, causes the wire to vibrate. The wire vibrating in front of Coil B varies the magnetic flux through the coil thus inducing a voltage in it the frequency of which is the same as that of the vibrating wire. This voltage is applied to the grid of the tube, which in turn controls the current in the driving Coil A. Therefore the wire vibrates at its natural frequency, which depends entirely on the tension, which in turn depends on the pressure on the cell.

The buffer tube, a No. 27, is coupled to the driving tube by a 0.01 mfd. condenser and a 200,000 ohm potentiometer, R_2. The purpose of the buffer tube is to prevent any possibility of the oscillator pulling the wire into synchronism when the frequencies of the oscillator and of the wire are nearly the same.

The output of the buffer tube is connected in series with the output of a variable frequency oscillator and a pair of phones. The note heard in the phones, when the wire is vibrating and the oscillator operating, is the "beat-note" between the two frequencies. When the frequency of this "beat-note" is zero, then the frequency of the oscillator is the same as the frequency of vibration of the wire. The oscillator used in the preliminary tests was a simple Hartley Oscillator, the frequency of which is varied by means of a decade condenser and a continuously variable condenser.

The cell is calibrated as follows: First the frequency of the oscillator is set at some value near that of the wire by means of a tuning fork. This is done with the condenser readings set at some selected value, and the correct frequency is obtained by varying the coupling between the coils in the oscillator. Periodically this setting should be checked to make sure that the frequency of the oscillator is correct for a particular setting of the condensers. After this check is made, the output of the buffer and the phones are connected in series with the output of the oscillator. With no load on the cell, the frequency of the oscillator is varied until it is the same as the frequency of the wire, and the condenser readings are taken. Now a load is applied to the cell and the operation repeated.

The load on the cell is plotted against the condenser readings; this gives a calibration curve.

Since the frequency of the oscillator may vary with any voltage variation, a stabilized oscillator, similar to that shown on page 285 in "Measurements in Radio Engineering" by Terman, would be more satisfactory.

All the equipment shown in Fig. 2, except the wire and Coils A and B, which are in the cell, are contained in a steel cabinet, together with a power supply. The four wires from the cell are connected to a four prong plug which is plugged into a four prong socket mounted on the cabinet.

The oscillator and its power supply are contained in another cabinet equipped with suitable jacks for connecting the two outputs and phones in series.

The same equipment is used to operate any number of cells, merely by plugging in each one separately. The mechanical set-up, capable of giving the required load range which was used for calibration, is shown in Fig. 3.

This simple arrangement is sufficiently indicated to require no written descrip-
tion.   In this work care was taken to approach the beat-note always from the
same side of the cell note.
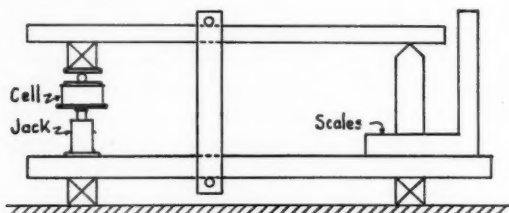
FIG. 3

Fig. 4 shows a typical calibration curve.   For similar initial conditions the
curve repeats fairly well.   From it, when an unknown load is applied to the
cell (the capacity of the condensers having been determined from the readings
on the dials) the magnitude of the applied load is at once determined.
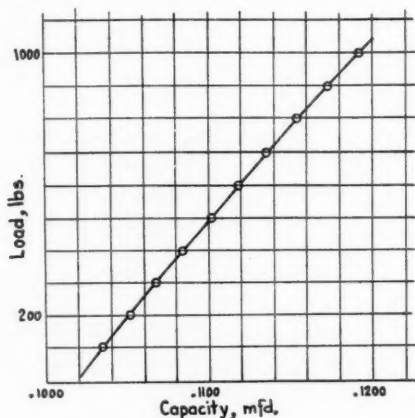
FIG. 4

The condenser set used in the tests can be improved considerably and will
lead to greater accuracy of readings.   The cell exhibits remarkable sensitivity,
for a change in beat-note due to application of the fingers to the cell can be
heard.   There is every indication that the accuracy of this cell will be quite
satisfactory for the purpose of the measurement of earth pressure and that
its rugged construction, as well as its capacity for remaining in working con-
dition over long periods, will make it pre-eminently suitable for that purpose.

Acknowledgment

CO-ORDINATION COMPOUNDS OF 1 : 3-DIAMINOISOPROPANOL[1]

BY J. G. BRECKENRIDGE[2] AND J. W. R. HODGINS[3]

Abstract

1 : 3-Diaminoisopropanol combines with cobaltous salts to give a series of cobaltic co-ordination compounds, which had been previously prepared by the use of roseo-cobaltic salts. The base has also been found to give crystalline co-ordination compounds with cupric, silver, and zinc salts.

The co-ordination compounds of 1 : 3-diaminoisopropanol have been investigated by Mann (6), who obtained stable compounds with cobaltic cobalt and nickel. Since that time the interesting series of co-ordination compounds of the ethanolamines with cobaltous cobalt were investigated by Hieber and Levy (4, 5), Duff and Steer (1), Garelli and Tettamanzi (2), and Tettamanzi and Carli (8). As stable co-ordination compounds of cobaltous cobalt with aliphatic amines were desired for another purpose, it was thought possible that compounds similar to those with the ethanolamines might be prepared from diaminopropanol. This proved not to be the case, the compound obtained by interaction of the diamine with cobaltous chloride being similar to that obtained by Mann (6) from the diamine and roseo-cobaltic chloride. It was evident that spontaneous oxidation had taken place, this phenomenon being a characteristic of co-ordinated cobaltous salts.

However, it was not immediately apparent that the two compounds were identical, since the crystals were dissimilar, and on drying over phosphorus pentoxide *in vacuo* at 100° C. the writers' compound lost water corresponding to $2H_2O$. The compound prepared by Mann (6) had not been dried in this manner, and thus there was no record of this behaviour. The structure assigned by Mann to his series of compounds was (I), and in view of the apparent distinction between the two, the writers thought it possible that their series of compounds might contain cobaltous cobalt, and would then be represented by (II). Elementary analysis could not decide the point, since the two formulae differ by only one hydrogen atom.

$$
\text{I} \quad
\begin{bmatrix}
& & \text{OH} & & \\
\text{CH}_2\text{NH}_2 & & | & \text{NH}_2\text{CH}_2 & \\
\text{CHOH} & & \text{Co} & \text{HOCH} & \\
\text{CH}_2\text{NH}_2 & & | & \text{NH}_2\text{CH}_2 & \\
& & \text{OH} & &
\end{bmatrix}^{+}
$$

$$
\text{II} \quad
\begin{bmatrix}
\text{CH}_2\text{NH}_2 & & \text{NH}_2\text{CH}_2 \\
\text{CHOH---} & \text{Co} & \text{---OCH} \\
\text{CH}_2\text{NH}_2 & & \text{NH}_2\text{CH}_2
\end{bmatrix}^{+} \cdot 2\text{H}_2\text{O}
$$

$$
\text{III} \quad
\begin{bmatrix}
\text{CH}_2\text{NH}_2 & & \text{NH}_2\text{CH}_2 \\
\text{CHO---} & \text{Co} & \text{---OCH} \\
\text{CH}_2\text{NH}_2 & & \text{NH}_2\text{CH}_2
\end{bmatrix}^{+}
$$
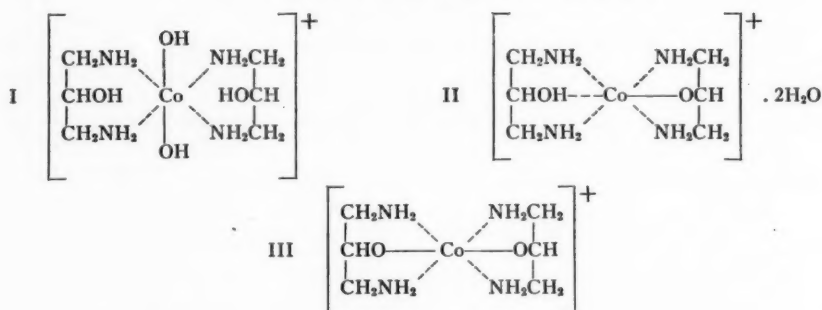
On re-investigation of Mann's compound, it also was found to lose two molecules of water on drying as described, to give a product of appearance identical to the writers'. Also, a series of compounds prepared from cobaltous salts and the diamine all lost exactly two molecules of water on drying, and since it is unlikely that they would all contain two molecules of water of crystallization (especially the thiocyanate), another explanation was sought.

It will be seen that in a compound of formula I, two molecules of water may be lost from the two "free" hydroxyl groups and the hydrogens of the alcoholic hydroxyl groups, giving a product of formula III. In this case, all six co-ordination positions of the cobalt atom are taken up by bridged groups, but it is difficult to imagine any other structure. The stereochemistry of this ion will be precisely similar to that of cobalt and α,β,γ-triaminopropane, described by Mann and Pope (7), when only one of the three theoretically possible isomerides could be isolated.

There remained to be explained the different crystalline forms of the compounds prepared by means of the two methods. The compound obtained from roseo-cobaltic chloride crystallized in small needles, whereas the compound from cobaltous chloride appeared as monoclinic prisms. It was thought at first that this difference might be due to (a) dimorphism, or (b) cis-trans isomerism, since in (I) the two "free" hydroxyl groups may occupy adjacent or opposite corners of the octahedron. However, a crystallographic examination (reported in the Experimental section) showed that the crystals differed only in habit, and were otherwise identical. It was thus evident that the compounds prepared by means of different methods were the same, but the transformation of (I) into (III) on drying was thought sufficiently novel to be worth while placing on record.

Metals other than cobalt were also investigated, copper, silver, and zinc giving crystalline products. The compounds with cupric salts were deep violet, and were of the general formula [Cu dap$_2$]X$_2$, with the copper atom in the normal 4-co-ordinated state. An unstable crystalline silver salt was isolated, having the formula AgNO$_3$. dap. The salts formed with the zinc halides were in a few cases well crystallized, but analysis produced no definite results for a simple compound, and they could not be recrystallized without altering their empirical formula.

Experimental

1 : 3-Diaminoisopropanol (Eastman Kodak Co. Practical grade) was purified either through the hydrochloride, as in the purification of triethanolamine by Germann and Knight (3), or by one distillation *in vacuo* in an all-glass apparatus (b.p. 113° C. at 4 mm., 132° at 14 mm.). It was stored in a desiccator over soda-lime.

Cobalt Compounds—General Formula $[(C_3H_9N_2O)_2Co]X$

Ten grams of $CoCl_2 . 6H_2O$ (or the equivalent of anhydrous salt) in 200 cc. 95% ethanol was added to 20 gm. of base (3 moles + excess) in 100 cc. 95% ethanol, and the mixture shaken. An exothermic reaction took place, and a reddish oil appeared, which crystallized on further shaking. The product was filtered, washed with ethanol, and recrystallized from water, giving well formed, clear red crystals in nearly theoretical yield. On drying over phosphorus pentoxide *in vacuo* at 100° C. water was lost; this left salmon-pink crystals with a bronze lustre, which broke down very readily to a powder.

Similar compounds were prepared from cobaltous bromide, iodide, and nitrate, the thiocyanate by treating a water solution of the iodide with potassium thiocyanate, and the camphor-10-sulphonate and the α-bromocamphor-π-sulphonate by interaction of the iodide and the silver salt of the camphor sulphonic acid. All these compounds were similar in appearance to the cobalt chloride compound, and behaved in the same manner on drying.

The analytical figures for the dehydrated compounds are given in Table I.

A sample prepared from the base and roseo-cobaltic chloride, as described by Mann (6), lost water corresponding to $2H_2O$ on drying:—calcd., 11.7%;

TABLE I

Compound	Mol. wt.		Cobalt, %	Halogen, %	Nitrogen, %	Loss on drying, %
Chloride	272.7	Calcd.	21.6	13.0	20.5	11.7
		Found	21.2	12.9	20.2	11.5
Bromide	317.1	Calcd.	—	25.2	17.7	10.2
		Found	—	24.9	17.6	9.9
Iodide	364.1	Calcd.	16.2	34.8	15.4	9.0
		Found	16.4	34.6	15.3	9.2
Thiocyanate	295.3	Calcd.	—	—	23.7	10.9
		Found	—	—	23.4	11.1
Nitrate	299.2	Calcd.	—	—	23.4	10.8
		Found	—	—	23.6	10.6
d-Camphor-10-sulphonate	468.3	Calcd.	—	—	11.9	7.2
		Found	—	—	11.8	7.2
d-α-Bromocamphor-π-sulphonate	547.2	Calcd.	—	—	10.2	6.2
		Found	—	—	10.1	6.3

found, 11.6%.   In all respects except the appearance of the crystals this was similar to the compound prepared directly from cobaltous chloride.

Specimens of the crystals of the chloride prepared by the two methods were submitted to Dr. M. A. Peacock of the Department of Mineralogy for crystallographic examination, and he reports as follows—

"Monoclinic: $a : b : c = 1.134 : 1 : 0.861$; $\beta = 110° 27'$

Forms: $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $q\{\bar{1}11\}$.

Twin planes: (100) on some crystals.

Measured angles:	Sample A		Sample B	
Face	φ	ρ	φ	ρ
$c(001)$	90° 00'	20° 27'	90° 00'	20° 25'
$m(110)$	43° 12'	90° 00'	43° 10'	90° 00'
$q(\bar{1}11)$	−26° 53'	43° 31'	−24° 39'	43° 57'

"The crystals from Samples A and B give practically the same angles, but they differ in habit.   Sample A (prepared from cobaltous chloride) are prismatic with large m, narrow a and b, q larger than c, and always twinned on (100).   Sample B (prepared from roseo-cobaltic chloride) are single individuals with large m, narrow a and b, large c, and very narrow q, which gives very poor signals."

Copper Compounds—General Formula $CuX_2 . (C_3H_{10}N_2O)_2$

Cupric chloride (1 mole) in 95% ethanol added to excess base in ethanol gave a dark blue solution, which in a few minutes deposited a blue oil.   This crystallized on shaking, giving a lilac-coloured microcrystalline compound, very soluble in water, and only slightly soluble in ethanol.   The product was recrystallized from 90% ethanol; this gave deep violet crystals, which decomposed on heating at 181° C.   The yield was nearly theoretical.   A similar product was prepared from copper bromide.   Copper nitrate gave a product of the same appearance, but with a decomposition point of 160° C., after softening at 135° C.   There was no loss of weight on drying the above-mentioned compounds over phosphorus pentoxide *in vacuo* at 100° C.   The analytical figures are given in Table II.

TABLE II

Compound	Mol. wt.		Copper, %	Halogen, %	Nitrogen, %
Chloride	314.7	Calcd.	20.2	22.5	17.8
		Found	20.3	22.3	17.6
Bromide	403.6	Calcd.	15.8	39.6	13.9
		Found	16.1	39.6	13.7
Nitrate	367.8	Calcd.	—	—	22.8
		Found	—	—	22.9

Silver Compound

Silver nitrate (3 gm.) in 80 cc. of 95% ethanol was added gradually to 1.6 gm. of base in 50 cc. of 95% ethanol, with stirring and cooling. On standing, the milky solution deposited small white needles, which were filtered and washed with ethanol. The compound was unstable, and began to decompose within a few hours. Calcd. for $C_3H_{10}N_2O . AgNO_3 . 0.5H_2O$: Ag, 40.1, N, 15.6%. Found: Ag, 40.2, 40.1; N, 15.3, 15.6%. When absolute ethanol was used as the reaction medium, crystallization was very slow.

Zinc Compounds

Zinc chloride in 95% ethanol was mixed with excess base in ethanol and the mixture allowed to stand. An oil appeared which crystallized very slowly, giving hard clear white crystals. These were filtered, washed, and dried. Analysis gave the following: Zn, 17.7; Cl, 14.4; N, 17.0%. This does not correspond to any simple formula for the product. The product was recrystallized from water (very soluble), and the microcrystalline product gave the following figures: Zn, 34.4, 34.3; Cl, 18.8, 18.8%. Calcd. for $C_3H_9N_2O$. ZnCl: Zn, 34.4; Cl, 18.7%. These figures remained unchanged when the compound was again recrystallized from water, but when washed with alcohol the percentage of chlorine became 30.7%, and the compound did not appear to be homogeneous.

Similar results were obtained with the product from zinc iodide and the base—the analytical figures were altered on recrystallization, and it seemed likely that hydrolysis was taking place.

Acknowledgments

References

1. DUFF, J. C. and STEER, E. H.   J. Chem. Soc. 2861-2862.   1932.
2. GARELLI, F. and TETTAMANZI, A.   Gazz. chim. ital. 63 : 570-575.   1933.
3. GERMANN, F. E. E. and KNIGHT, O. S.   J. Am. Chem. Soc. 55 : 4150.   1933.
4. HIEBER, W. and LEVY, E.   Ann. 500 : 14-34.   1932.
5. HIEBER, W. and LEVY, E.   Z. anorg. allgem. Chem. 219 : 225-237.   1934.
6. MANN, F. G.   J. Chem. Soc. 2904-2918.   1927.
7. MANN, F. G. and POPE, W. J.   J. Chem. Soc. 2675-2681.   1926.
8. TETTAMANZI, A. and CARLI, B.   Gazz. chim. ital. 64 : 315-321.   1934.

THE ACTIVITY OF WATER IN SULPHURIC ACID SOLUTIONS AT 25° C. BY THE ISOPIESTIC METHOD[1]

By H. Sheffer[2], A. A. Janis[3], and J. B. Ferguson[4]

Abstract

The activities of water in aqueous solutions of sodium chloride and of sulphuric acid have been compared by the isopiestic method at 25° C. over a range of molalities extending up to that of the saturated salt solution. The apparatus, which was of the Sinclair type, proved to be as efficient as any yet devised. The results remove the uncertainties that previously existed in regard to the position of the m_1/m_2 curve and give a qualitative indication of the second dissociation of sulphuric acid. The calculated activities agree with the best available data. The isopiestic standard chosen by Janis and Ferguson has been confirmed over the whole molality range.

Introduction

In an earlier paper, a sodium chloride standard for isopiestic measurements was proposed by Janis and Ferguson (7). Comparisons of solutions of sodium and of potassium chlorides at 25°, 30°, and 35° C. confirmed the selections made by them over the possible range of molalities. An attempt was made to confirm the selections at the higher molalities by a study of sulphuric acid solutions. The confirmation was as good as the available data on the acid would warrant, but there were certain discrepancies between these results and those of Scatchard, Hamer, and Wood (8) whose paper appeared just as the writers' paper was being sent to press. The results of these other investigators were not themselves entirely concordant, and it appeared desirable to re-investigate this acid over a wide range of molalities. This was especially so since there was a possibility that new vapour tension measurements on the stronger acid solutions might be available in the near future and the present uncertainty in our knowledge of these solutions thereby removed.

Experimental

The apparatus and procedure were essentially those described by Janis and Ferguson for the small silver dishes. A 6 in. desiccator containing a $5\frac{1}{2}$ in. copper block with depressions for four dishes proved more efficient than the larger apparatus previously used. The block rested on a layer of paraffin wax which held it in position and also thermally lagged it.

The dishes were placed directly in the depressions in the block without the use of any liquid in the latter. Dishes with similar solutions were placed in diagonally opposite positions. The evacuation was carried out carefully to

prevent spattering, the formation of large bubbles being avoided. Evaporation losses were controlled by a careful re-fitting of the lids when necessary by the manufacturer and by weighing the worst dishes first. They did not exceed 0.0005 gm. per dish. All weights were corrected to *in vacuo*. Whenever the weight was large enough, the dried salt was weighed directly into the cleaned dishes. In all other cases, known solutions of salt and of acid were either weighed in the dishes or added to the dishes from weight burettes.

The apparatus was tested by the use of four dilute solutions, the maximum difference in the molalities being about 4%. After two weeks the final molalities of these brines were 0.08999, 0.09012, 0.09014, and 0.09015. The writers' experience seems to show that the evacuation materially aids in the attainment of equilibrium and undoubtedly is a disturbing factor in rate experiments. However, it is unreasonable to suppose that an agreement in final molalities like that just given could arise from simple pumping, with the attendant disturbance of temperature conditions. The experiments lasted from 24 hr. for the stronger solutions to two weeks for those at and below 0.1 m. Twenty-four hours was not sufficient for experiments in which the salt solutions contained solid salt, owing, no doubt, to the fact that in this case several processes were taking place simultaneously.

In all experiments the sodium chloride was from the same lot as that used by Janis and Ferguson, and the water was conductivity water. Salt solutions were made up by weight from salt carefully dried at 600° C. The original acid solutions from which weight dilutions were made were themselves analyzed by weight titration using sodium carbonate and phenolphthalein. The procedure was essentially that of Hillebrand and Lundell (5). The carbonate was prepared from the recrystallized bicarbonate by heating to constant weight in an atmosphere of carbon dioxide at 600° C. Four samples of acid were compared. These are respectively: *(a)*, B.D.H. Analar; *(b)*, Acid *(a)* redistilled by Janis; *(c)*, Acid *(a)* redistilled by Janis and Sheffer; and *(d)*, Grasselli c.p. acid redistilled by Shankman (3). The distillations were carried out in an all-glass apparatus at a reduced pressure in a stream of nitrogen, and the middle third portion was taken. Acid *(b)* was used in the earlier work and Acid *(c)* in the final measurements. The isopiestic molalities were respectively: *(a)* 4.379; *(b)* 4.381; *(c)* 4.371; and *(d)* 4.370. The difference between the molality of *(b)* and of *(c)* was confirmed by two rather extensive series of isopiestic measurements only the second of which is reported in this paper. There must have been some slight difference in the original acids, which came from different bottles, and it would appear that the earlier distillation did not remove the last trace of impurities.

Results and Discussion

The isopiestic molalities of sodium chloride and of sulphuric acid solutions are given in Table I, together with the values of the activities of water in these solutions. The latter were obtained from the values of R listed by Janis and

TABLE I

ISOPIESTIC MOLALITIES AND THE ACTIVITY OF WATER IN SOLUTIONS OF SULPHURIC ACID
AT   25° C.

m_1 Sulphuric acid		m_2 Sodium chloride		a_1 Activity	m_1 Sulphuric acid		m_2 Sodium chloride		a_1 Activity
4.349	4.351	(6.145)*		0.7530†	0.7338	0.7331	0.8174	0.8166	0.9729
4.348	4.347	6.142	(6.145)*	0.7531	0.6403	0.6398	0.7066	0.7065	0.9766
3.815	3.814	5.255	5.255	0.7936	0.5200	0.5193	0.5675	0.5675	0.9813
3.154	3.157	4.229	4.231	0.8404	0.3843	0.3841	0.4158	0.4162	0.9863
2.830	2.829	3.728	3.730	0.8628	0.2865	0.2868	0.3089	0.3089	0.9898
2.184	2.182	2.770	2.770	0.9023	0.1882	0.1880	0.2031	0.2032	0.9934
1.544	1.544	1.859	1.859	0.9367	0.0958	0.0957	0.1041	0.1042	0.9966
1.269	1.266	1.488	1.486	0.9500	0.04557	0.04545	0.0508	0.0511	0.99830
1.046	1.045	1.201	1.201	0.9598	0.01872	0.01880	0.02423		0.99918
0.8826	0.8814	0.9959	0.9959	0.9669					

* Saturated solution.
† Gordon reports 0.7532 for a_1 , based upon a new vapour pressure measurement by Shankman.

Ferguson.   For this purpose it is convenient to use a deviation curve based
on the deviation of the values of the activity from those given by a linear
function of the salt molality.   This curve is itself linear in m_2 (NaCl) at the
higher concentrations and therefore permits extrapolation to the saturated
solution molality with a minimum of error.   A plot of m_1/m_2 is shown in
Fig. 1.   The results of Scatchard, Hamer, and Wood are also included, the
ratios having been calculated by us from their tabulated molalities.   Several
determinations that were too close together to plot separately are shown by
a circle with lines indicating the number of measurements.   Information
concerning our duplicates is given in the table.   For the saturated salt solution
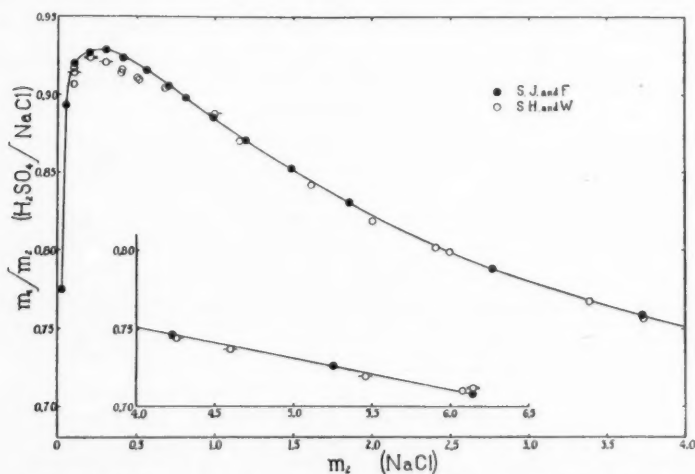

Fig. 1. The isopiestic molalities of solutions of sodium chloride and of sulphuric
acid at 25° C.

their ratio is 0.7120, whereas our ratio is 0.7080, and the latter value agrees with their value at 6.0781 m. The molality of the saturated solution is given in I.C.T. (6) as 6.145; their isopiestic values range from 6.1429 to 6.1461, and our result is 6.142. The greatest discrepancy between the two series of results occurs below 0.5 m, and it was at this point that they altered their procedure. If the lowest point at 0.1 m is neglected, the difference here amounts to a vapour pressure difference of 0.0003 mm. of mercury.

A consideration of the Debye-Hückel and of the Duhem-Margules equations suggests that the ratio m_1/m_2 should approach the limiting value of 0.66 if the acid is a ternary electrolyte at great dilution. The high value that this ratio attains can mean only that the acid is essentially a binary electrolyte over most of the range investigated and becomes ternary only in dilute solution. Our curve indicates that but little of the second dissociation of sulphuric acid occurs above 0.2 m and that it increases rapidly below 0.1 m. This agrees with the experimental results and the conclusions of Dawson (1) in respect to this dissociation.

The activities of the water in sulphuric acid solutions at rounded molalities are given in Table II. The first column gives our values which were obtained from the experimental values by means of a sensitive deviation curve. The second column contains values calculated by us from the tabulated values of φ given by Scatchard, Hamer, and Wood. The latter values are not due to isopiestic measurements alone but represent their opinion of the best values indicated by the then available data. In Column III are given the rounded values of Gordon (3), which are based on the new vapour pressure measurements of Shankman. The details of this work will be published elsewhere in the near future. Harned and Hamer (4) calculated some of these activities from their e.m.f. measurements, and these are given in the fourth column.

The only serious differences occur at the higher molalities where our results agree with those of Gordon. The sodium chloride standard of Janis and Ferguson was originally confirmed in part by the use of potassium chloride

TABLE II

THE ACTIVITY OF WATER IN SOLUTIONS OF SULPHURIC ACID AT 25° C.

m_1 Sulphuric acid	a_1 S.J.F.	a_1 G.	a_1 S.H.W.	a_1 H.H.	m_1 Sulphuric acid	a_1 S.J.F.	a_1 G.	a_1 S.H.W.	a_1 H.H.
0.05	0.99814			0.99819	1.2	0.9530		0.9532	
0.1	0.99639		0.9964	0.9964	1.4	0.9440		0.9439	
0.2	0.9929		0.9928		1.5	0.9392			
0.3	0.9893		0.9892		1.6	0.9344		0.9341	
0.4	0.9858		0.9856		1.8	0.9240		0.9237	
0.5	0.9821		0.9819	0.9821	2.0	0.9128	0.9129	0.9129	0.9136
0.6	0.9783		0.9781		2.5	0.8837	0.8838	0.8837	
0.7	0.9743		0.9743		3.0	0.8513	0.8514	0.8514	0.8506
0.8	0.9703		0.9703		3.5	0.8164	0.8164	0.8161	
0.9	0.9662		0.9662		4.0	0.7797	0.7795	0.7781	
1.0	0.9620		0.9620	0.9620	5.0		0.7032		0.6980

solutions. It has now been confirmed over the whole range from $0.1\ m$ to $6.0\ m$ by the use of sulphuric acid solutions. Since the work of Gibson and Adams (2) was used to fix the standard at the high molalities, it is apparent that their measurements are in entire agreement with those of Shankman and Gordon.

The values for the activity of water in the acid solutions at molalities below $0.1\ m$ were calculated on the assumption that the plot of a_1 against m_2 for sodium chloride was linear between $m_2 = 0$ and $m_2 = 0.1$. A similar assumption in respect to sulphuric acid would yield a value at $0.05\ m$ of 0.99820, which agrees with the value of Harned and Hamer of 0.99819. If the first assumption is correct then these values would correspond to a ratio of m_1/m_2 of 0.93. That this must be incorrect is evident from an inspection of Fig. 1; the position of the ratio curve indicates the reason for our lower value of 0.99814.

Acknowledgment

The writers wish to thank Dr. A. R. Gordon and Dr. S. Shankman for the use of their unpublished results.

References

1. DAWSON, H. M. Proc. Leeds Phil. Lit. Soc., Sci. Sect. II. 359-364. 1933.
2. GIBSON, R. E. and ADAMS, L. H. J. Am. Chem. Soc. 55 : 2679-2695. 1933.
3. GORDON, A. R. and SHANKMAN, S. Informal communication.
4. HARNED, H. S. and HAMER, W. J. J. Am. Chem. Soc. 57 : 27-33. 1935.
5. HILLEBRAND, W. F. and LUNDELL, G. E. F. Applied inorganic analysis. John Wiley and Sons, New York. 1929.
6. INTERNATIONAL CRITICAL TABLES, VOL. IV. McGraw-Hill Book Co., New York. 1928.
7. JANIS, A. A. and FERGUSON, J. B. Can. J. Research, B, 17 : 215-230. 1939.
8. SCATCHARD, G., HAMER, W. J., and WOOD, S. E. J. Am. Chem. Soc. 60 : 3061-3070. 1938.

A NEW VACUUM ADIABATIC CALORIMETER[1]

By A. B. Adams[2], R. S. Brown[3], W. H. Barnes[4], and O. Maass[5]

Abstract

A new adiabatic calorimeter is described in which transfer of the material under investigation from the thermostat to the calorimeter is effected through an evacuated space.

Introduction

In two earlier papers (1, 2) it was mentioned that a new adiabatic calorimeter was under consideration in the hope of continuing certain specific heat investigations with a higher degree of accuracy. The previous calorimeter (2, p. 212) had been developed to a stage where the accuracy of total heat measurements became dependent upon the technique of transferring the container and contents from the thermostat (at the desired initial temperature) to the calorimeter. As is usual in the case of many adiabatic calorimeters, this transfer was made through the air of the room, and the total heat measurements were thus subject to errors introduced by varying conditions of room temperature and humidity. Although attempts can be made to introduce corrections for these effects, such correction factors are always somewhat uncertain. It was deemed advisable, therefore, to eliminate the source of error by arranging for the transfer of the container through an evacuated space. It is with a description of this new vacuum adiabatic calorimeter that the present paper is concerned.

Description of the Calorimeter

A diagrammatic cross section of the calorimeter (not drawn to scale) is shown in Fig. 1.

The brass calorimeter jacket, A, is supported on metal legs inside a large galvanized iron vessel, B, of approximately 18 litres capacity. Filled with water, this vessel constitutes the adiabatic shield. The temperature is controlled by the addition of hot or cold water from jets of suitable sizes distributed conveniently around the rim of the vessel, B. Particular attention was paid to the stirring of this bath in order to avoid lag in the equalization of the temperature of the jacket wall. Efficient stirring is effected by four large double-bladed stirrers, alternate stirrers rotating in opposite directions.
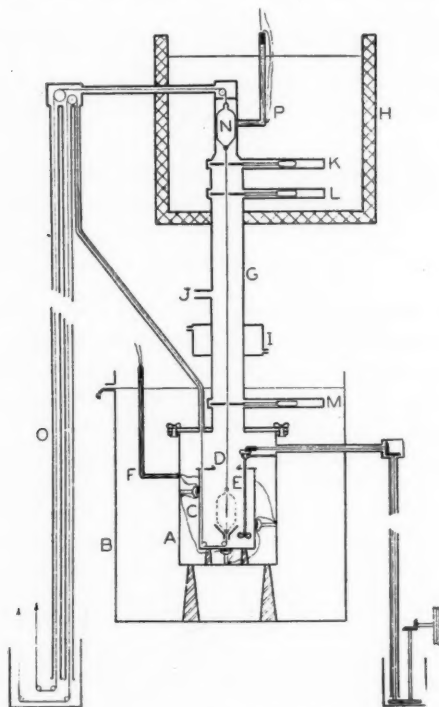
FIG. 1.   *Vacuum adiabatic calorimeter.*

The calorimeter inner vessel, *C*, is of mild steel, highly polished, and has a capacity of about 500 cc.   It is supported on three slender ebonite legs at a distance of 2 cm. from the bottom and walls of the calorimeter jacket.   Since the calorimeter is operated with this space evacuated, the 2 cm. gap gives a sufficiently low thermal leakage modulus.

Owing to vacuum conditions, mercury is employed as the calorimetric liquid.   The high density of mercury, of course, results in a much larger heat capacity for the calorimeter, and thus a smaller temperature change for a given quantity of heat introduced or removed than that for the same volume of water.   Against this factor, however, may be set the advantage of eliminating the corrections necessitated by evaporation or condensation of the calorimetric liquid during temperature changes in the calorimeter (2, p. 208).

The thin cover, *D*, also of mild steel, is designed to permit free passage of the container, stirrer, and threads, and yet prevent loss of mercury due to splashing when the container is drawn rapidly into the inner calorimeter vessel.

The mercury in the inner vessel is stirred by means of a glass blade stirrer, *E*, with a very thin shaft; this reduces heat conduction to a minimum.   The

stirrer is rotated by a geared shaft passing out through the bath, B, so that its temperature always is the same as that of the calorimeter environment. Outside the bath, the drive is geared through a vertical shaft, 90 cm. long, which terminates in a reservoir of mercury. The casing of this shaft is vacuum tight, so that, when the calorimeter is evacuated, mercury rises in the casing to form an effective seal. The drive is operated by a controlled motor. The stirring of the calorimetric liquid is so regular and the time-temperature curves for each experiment are so smooth that it has not been necessary to employ synchronous stirring.

Between the calorimeter jacket and the inner vessel, nine pairs of copper-constantan thermels are arranged; eight in the form of a helix about the calorimeter vessel and one at the bottom. In this way, the temperature over the whole surface is integrated. The thermels are of the radiation type previously described (1). In the present calorimeter, the suspended junctions are at a distance of about 2 mm. from the wall of the inner calorimeter vessel. The thermel-galvanometer circuit is protected from the effects of stray electrical currents and unequal temperatures at the galvanometer binding posts in the same way as before (1, p. 72). The sensitivity of the present Leeds-Northrup D'Arsonval galvanometer is 11 mm. per microvolt at a distance of 1 m. The coil resistance is 18 ohms. With the present optical path of about 2.5 m., a deflection of 1 mm. on the mirror scale corresponds to a temperature difference of $0.00019°$ C. between the inner calorimeter vessel and the outer bath when the calorimeter is not evacuated, and to a difference of $0.00021°$ when the calorimeter is evacuated. The temperature of the outer bath can be maintained to within $0.0002°$ of that of the inner vessel for long periods of time without any difficulty.

The top of the calorimeter jacket, A, and its cover are flanged and held together by a number of wing nuts. An ungreased rubber gasket forms an effective seal. This gasket was cut to the exact shape of the flanged top of the jacket, and was rubbed into a wedge towards its inner circumference in order to relieve strain on the soldered joins between flange and jacket when the wing nuts are tightened.

From the cover, a brass tube, G, 3.5 cm. in diameter, leads into the thermostat, H, above the calorimeter proper. It is so constructed that when the container is drawn into the thermostat it makes good thermal contact with the walls of the tube, whereas it does not touch them during its passage to and from the calorimeter. A water cooler, I, is provided on the tube but was found to be unnecessary in the present work. The apparatus is evacuated at J.

To prevent radiation between the thermostat and the calorimeter proper, three steel shutters, K, L, M, are situated along the tube, G. The shutter, M, cuts out radiation into, or from, the inner calorimeter vessel by way of tube, G. The shutters K and L shield the container by isolating it when it is in position in the thermostat. A small piece of iron is attached to the handle of each shutter. A solenoid electromagnet (not shown in Fig. 1) is

placed around the tube containing the arm of each shutter, so that by moving the magnet the shutter is drawn back and forth. A slit in each shutter permits passage of a thread, attached to the container, down the centre of the tube. The shutters are so arranged that, in the closed position, the slits are not parallel, and hence only a small opening down the centre, and occupied by the thread, remains. Tests made with the container in the thermostat and in the calorimeter and with the shutters open and closed have indicated conclusively that the shutters effectively cut out all radiation between the two sections of the apparatus.

The thermostat, H, consists of two concentric galvanized iron vessels. The outer one is approximately 2 in. greater in diameter and depth than the inner. The space between the two is filled with cork dust for thermal insulation. The thermostat has a capacity of about 12 litres. For initial temperatures above that of the room it is filled with glycoline and is heated electrically. The electric heaters consist of the element of an electric iron cut in half and soldered into thin copper envelopes. Such heaters are quite inexpensive to make and have proved to be remarkably free from lag. When the calorimeter is not in use, and also between runs, the thermostat is controlled by a large toluol thermoregulator working in conjunction with a sensitive relay. The toluol bulbs of the thermoregulator are fitted with copper gauze crosses throughout their length in order to ensure rapid attainment of equilibrium and consequently a minimizing of lag. The temperature of the thermostat is thus controlled to within $\pm 0.02°$ C. For the half hour preceding the introduction of the container into the calorimeter, however, the thermostat is regulated by hand to within $\pm 0.005°$ C. Efficient stirring is effected by means of a large triple-blade stirrer. The thermostat was tested with a movable set of thermels, and nowhere throughout the bath was a temperature gradient greater than $0.01°$ observed.

The platinum container, N, has a capacity of approximately 24 ml. It is "streamlined" to minimize splashing of mercury as it is drawn rapidly into the calorimeter, and to prevent mercury from being carried out of the calorimeter inner vessel as the container is returned to the thermostat. Transfer of the container is effected by means of a flax thread attached to either end of it and passing over the system of pulleys indicated in Fig. 1. The long columns, O, terminate in a mercury reservoir to provide a vacuum seal. From this reservoir the threads pass around a large, mounted wheel of approximately 32 in. diameter, to which they are fastened. A quarter revolution of this wheel effects the transfer of the container from the thermostat to the calorimeter. Its size is designed to afford complete control of the container during its rapid transit. A small weight is affixed to the wheel to hold the container beneath the surface of the mercury in the inner calorimeter vessel, C.

The thermocouple, P, was designed to indicate when the platinum container was in thermal equilibrium with the thermostat bath, and the approximate time required for equilibrium to be established. The inner junction was shielded to receive heat by radiation only from the container. The

outer junction was in thermal contact with the oil bath near the thermometer bulb.   The thermocouple was connected through clothes-pin switches to the same galvanometer as the lower set.   This thermocouple, however, did not serve the whole purpose for which it was intended.   At no time did it register zero deflection on the galvanometer while the thermostat was at an elevated temperature.   The direction of the deflection seemed to indicate that the container was permanently at a lower temperature than the thermostat.   The deflection was greater the higher the temperature of the thermostat, and when the thermostat was at room temperature, the deflection was zero. With an ice-water bath in the thermostat, a deflection in the opposite direction was observed.   The deflection was small when the apparatus was under atmospheric pressure but was markedly increased on evacuation.   Prolonged standing of the apparatus under reduced pressure did not cause the deflection to return to its original value; this indicates that the increased deflection was not a temporary effect set up on evacuation.   Similar phenomena were observed when the container was not in the thermostat; this indicates that it was not the temperature of the container which the thermel was recording. Electrically insulated thermal contact between the inner junction and the container decreased the deflection markedly.   The magnitude of the deflection indicated that a temperature difference of 0.1° C. existed between the two junctions of the thermel.   It has been mentioned previously, however, that the temperature gradient throughout the thermostat was never greater than 0.01°.

This anomalous behaviour could be explained if the column G (Fig. 1) were conducting heat away from the inner junction rapidly enough to maintain the junction at a lower temperature than the thermostat.   This did not seem probable, especially as an explanation of the increased deflection on evacuation.   Furthermore, by placing first a steam jacket, and then an ice jacket, about the column where it emerges from the thermostat, no change in the galvanometer deflection was observed.

The more probable explanation is that the thermel leads themselves conduct heat away from the junction.   This supposition receives support from a number of simple tests.   For example, the two junctions of a copper-constantan thermocouple were sealed into identical thin glass tubes, the junctions themselves being suspended in the centre of the tubes, while the double-silk-insulated leads from these junctions touched the walls throughout nearly all of their 10 in. length.   The two tubes were placed side by side in a Dewar flask filled with finely crushed ice and distilled water.   One tube was left at atmospheric pressure, the other was attached to a vacuum line.   Originally the junctions registered zero deflection, but, when one tube was evacuated, a deflection was observed; this indicated that this junction was warmer than that in the unevacuated tube.

The tubes then were placed in a Dewar bath at 50° C.   Again no deflection was observed with both junctions under atmospheric pressure, but, when

one tube was evacuated, the observed deflection indicated that this junction was colder than that in the unevacuated side.

With both junctions in a thermostat at room temperature, only a temporary deflection, which returned to zero in a few minutes, was obtained.

The results of these tests can be explained satisfactorily only by conduction of heat along the thermel leads.   In view of this fact, it was pointed out to workers with an electrical calorimeter in this laboratory that they might expect a similar effect along the leads used for their electrical input and voltage measurements of even greater magnitude, particularly at the temperatures produced by solid carbon dioxide in ether.   They subsequently found it necessary to run their wires through a copper lead-in tube, immersed in the bath, many times the original length employed.   In the case of the radiation thermels in the calorimeter proper, this difficulty does not arise since the lead-in wires and junctions are subject to the same environment.

In spite of its inability to indicate accurately any small temperature differences between the container and the thermostat, the thermocouple, P, did serve to show that temperature equilibrium is established between the container and the thermostat within 30 min.

Calibration of the Thermometers

The temperature of the outer bath of the calorimeter, and hence of the calorimetric liquid in the inner vessel, is determined by means of a platinum resistance thermometer, and a Mueller resistance bridge.   The same galvanometer is used in this circuit as in that of the radiation thermels.

The resistance thermometer was calibrated by measuring its resistance at $0°$ C. and at $100°$ C. in order to determine the fundamental interval.   The value of the constant δ was supplied with the thermometer.

The determination of the ice point was made by immersion of the thermometer to a depth of nine inches in a Dewar flask filled with finely crushed ice and distilled water.   Measurements were made with a current of 5 ma. through the thermometer.   The ice point was reproducible to within $\pm 0.001°$.

A new hypsometer was designed for the determination of the steam point. Steam from a constant-level generator passed through a short length of exposed glass tubing and bubbled through a few centimetres of water in a Dewar flask to ensure saturation and to guard against superheating.   The steam emerged from the Dewar flask through two insulated glass tubes that led to the hypsometer.   The hypsometer consisted of two concentric glass tubes about 30 in. in length and having diameters of $2\frac{1}{2}$ in. and $1\frac{1}{4}$ in. respectively. The outside wall of the outer tube was insulated and the tops of both tubes were closed.   The platinum thermometer was inserted to a depth of nine inches in the top of the inner tube.   Steam entered both tubes at the top, so that the inner tube was surrounded by a steam jacket and all air was expelled. Since both tubes were open at the bottom no pressure correction was necessary. Barometric readings were taken at the same times as the resistance measure-

ments. The boiling points of water at the observed pressures were obtained from the International Critical Tables (5). This hypsometer proved to be very sensitive and, if desired, could be employed satisfactorily for the accurate measurement of changes in barometric pressure.

The values for the constants of the present resistance thermometer are as follows: R_0, 25.52974 ohms; F, 9.9486; δ, 1.5.

In order to facilitate the determination of temperatures, the resistance of the thermometer is calculated, with the usual Callendar formula, at one-half degree intervals over the temperature range in which it is to be employed, and direct interpolation is made in these intervals where, for practical purposes, a linear temperature-resistance relationship may be assumed.

With the present five-dial Mueller resistance bridge and galvanometer circuit, the resistance of the platinum thermometer can be estimated to within 5×10^{-5} ohms. This corresponds to a deflection of 1.5 mm. on the mirror scale.

Beckmann thermometers are employed to determine the temperature of the thermostat. They are standardized, as required, against the platinum resistance thermometer.

Manipulation of the Calorimeter

The container is drawn into its upper position in the thermostat and the three shutters *(K, L, M)* are closed. The temperature of the thermostat is regulated automatically to within $\pm 0.02°$ of the desired initial temperature for at least one hour. Towards the end of this period, manual control of the thermostat to within $\pm 0.005°$ is started, the calorimeter is evacuated, and stirring of the inner and outer calorimeter vessels is begun. Adiabatic conditions are established and then maintained by running hot or cold water as required into the outer calorimeter bath. The temperature of the bath is measured at five-minute intervals to determine the first portion of the time-temperature curve of the inner calorimeter vessel. After about 30 min., and at a recorded time, the three shutters are opened and the container is drawn down to its lower position in the calorimeter. The time of transfer is less than 1 sec. The weight is attached to the wheel in order to keep the container in position below the mercury level in the inner calorimeter vessel and the lower shutter, M, is closed.

Immediately before drawing the container into the calorimeter, a large hot water jet is opened to the outer calorimeter bath. As soon as the container is in position in the inner calorimeter vessel, the temperature of the outer bath is regulated so as to follow as closely as possible the rapidly changing temperature of the inner calorimeter vessel. Temperature equilibrium of the inner vessel is established in about 15 min., after which time the temperature of the outer bath again is recorded at five-minute intervals to determine the last portion of the time-temperature curve.

Finally, the shutter, M, is opened, the container is drawn back to its upper position, and the three shutters are closed. Air, carefully dried to eliminate

effects of adsorbed moisture on subsequent evacuation, is admitted to the apparatus.   The temperature of the outer calorimeter bath, B, is reduced to about 10° below the starting temperature desired (so estimated that the final temperature of the inner calorimeter vessel after coming to temperature equilibrium with the container in the next experiment shall be approximately 25° C.).   In an hour the calorimeter is ready for another determination. Thus, once assembled, a large number of runs may be made under the same conditions without opening the apparatus at any point.

The Water Equivalent of the Calorimeter

Since the specific heats of certain of the materials of which the calorimeter is constructed (*e.g.*, glass and steel) are not known to a sufficient degree of accuracy, the water equivalent of the calorimeter was determined directly from a series of measurements with freshly boiled, distilled water in the container.   At the same time, the opportunity was taken of studying the effect of the vacuum and of different times of transfer of the container.   The results also indicate the degree of precision attainable with the apparatus in its present form.

The following sample data and calculations are typical of those involved in these determinations.

Wt. container, water, cement	= 74.6000 gm.
Wt. empty container	= 54.2875 gm.
Wt. water, cement	= 20.3125 gm.
Wt. cement	= 0.0051 gm.
Wt. water	= 20.3074 gm.
In vacuo correction	= 0.0215 gm.
Wt. water	= 20.3289 gm.
Initial temperature (thermostat)	
Beckmann thermometer	3.950°
Stem correction	0.031°
	3.981°
From standardization, this corresponds to	89.998° C.

Time-temperature Readings of Inner Calorimeter

Time, min.	0	5	10	10½*	30	35	40	45
Resistance, ohms	27.44095	27.44115	27.44135		28.07005	28.07045	28.07075	28.07105

* *Container introduced.*

From Time-temperature Curve (2, p. 206)

Resistance at time container introduced	= 27.44136 ohms
Extrapolation of last portion of curve back to time container introduced gives	28.06896 ohms
Increase in resistance	= 0.62760 ohms
This corresponds to a temperature rise of	6.2487° C.
Final temperature of inner calorimeter (corresponding to 28.06896 ohms)	= 25.211° C.

The temperature rise (6.2487° C.) in the calorimeter divided by the temperature drop (89.998 − 25.211 = 64.787° C.) of the container and contents and multiplied by 65 gives 6.2692° C. as the temperature rise in the calorimeter for a 65° drop in the temperature of the container and contents.

From the average specific heats of water (5, vol. 5, p. 232) and of platinum (6, vol. 2, p. 1246) between 90° and 25° C. and assuming a value of 0.4 cal. per gm. per deg. for the specific heat of de Khotinsky cement, the total heat given up to the calorimeter by the known weights of these materials is as follows: water, 1320.64 cal.; platinum container, 112.338 cal.; de Khotinsky cement, 0.133 cal.—a total of 1433.11 cal.

It will be observed that, by this method of calculation, the initial temperature and the final temperature automatically are corrected to 90.00° C. and 25.00° C., respectively. This involves the tacit assumption that the specific heats at these temperatures are essentially the same as those at the actual temperatures observed. The assumption is justified by the fact that in all determinations the real initial temperatures (*i.e.*, approximately 90°, 75°, 65°, 50° C., respectively) and the final temperature (approximately 25° C. in all cases) were much less than one degree from the corrected values.

Since a volume of 3.85 cc. of air was enclosed with the water in the container, it is of interest to examine the magnitude of the total heats due to the following: *(a)* heat capacity of the air, *(b)* heat capacity of uncondensed water vapour in the air space, *(c)* latent heat of condensation of vapour.

(a) Heat Capacity of Air

The volume of air at room temperature was 3.85 cc. Taking the density as 0.0012 and the specific heat as 0.2, the total heat given up to the calorimeter during the fall in temperature from 90° to 25° C. is 0.06 cal.

(b) Heat Capacity of Uncondensed Water Vapour

Taking the vapour tension of water at 25° C. as 23.76 mm. of mercury (5, vol. 3, p. 212), the weight of uncondensed water vapour in the air space at 25° C. is 0.00009 gm. Taking the average specific heat (C_p) of water vapour as 0.443 cal. per gm. per deg., the total heat given up to the calorimeter by the water vapour in the volume of 3.85 cc. during the fall in temperature from 90° to 25° C. is 0.0026 cal.

(c) Latent Heat of Condensation of Water Vapour

Taking the vapour tension of water at 90° C. as 525.75 (5, vol. 3, p. 212), the weight of water vapour in the 3.85 cc. air space at 90° C. is 0.00159 gm. Thus the weight of vapour that condenses during the fall in temperature from 90° to 25° C. is 0.0015 gm. Taking the average latent heat of evaporation as 563.55 cal. per gm. (5, vol. 3, p. 212), the total heat given up to the calorimeter owing to condensation of water vapour in the container during the fall in temperature from 90° to 25° C. is 0.85 cal.

Of these correction factors, *(a)* and *(b)* may be neglected in comparison with the total heat of the water, container, and cement (1433.11 cal.). Fur-

thermore, these two factors have increasingly smaller values for lower initial temperatures. The total heat brought down from each initial temperature must include, however, that due the latent heat of condensing vapour, *i.e.*, factor 3.

Hence the total heats given up to the calorimeter by the known weights of materials during a 65° drop in temperature are: water, 1320.64 cal.; platinum, 112.338 cal.; cement, 0.133 cal.; condensing vapour, 0.850 cal.; —a total of 1433.96 cal.

Dividing this total heat by the temperature rise (6.2692° C.) in the calorimeter gives 228.74 calories* per degree for the heat capacity of the calorimeter.

The results are summarized in Table I. The first column gives the number of the data for purposes of later identification. The second shows the corrected initial temperature of the container and contents. The third gives the time in seconds taken for the transfer of the container and contents from the thermostat to the calorimeter. The fourth indicates whether the apparatus was evacuated or not. The fifth records the number of determinations at each initial temperature. The sixth shows the heat capacity of the calorimeter. In each case the heat measurements have been corrected to a final temperature of 25.00° C. for the calorimeter.

TABLE I

HEAT CAPACITY OF CALORIMETER DETERMINED WITH DIFFERENT INITIAL TEMPERATURES AND UNDER DIFFERENT CONDITIONS OF TRANSFER

Data No.	T, °C.	Time, sec.	Evacuated (V) or not (A)	No. of runs	H. cal./deg.
1	90.00	1	V	19	228.74 ± 0.04
2	75.00	1	V	16	228.68 ± 0.05
3	60.00	1	V	12	228.63 ± 0.05
4	50.00	1	V	9	228.58 ± 0.03
5	90.00	3	V	7	228.75 ± 0.06
6	90.00	5 to 6	V	7	228.91 ± 0.15
7	90.00	1	A	7	229.24 ± 0.08
8	90.00	3	A	6	229.37 ± 0.25
9	75.00	1	A	8	228.96 ± 0.13
10	60.00	1	A	5	228.69 ± 0.11
11	50.00	1	A	2	228.62 ± 0.03

Discussion

An examination of Table I shows immediately that the most satisfactory results with the new calorimeter are obtained when it is evacuated and when transfer of the container from thermostat to calorimeter is effected rapidly. Thus, from data 1 and 5 an increase in the time of transfer from 1 to 3 sec.

* *Throughout this paper, quantities of heat are given in terms of the normal calorie.*

when the apparatus is evacuated does not alter the mean value for the heat capacity of the calorimeter, although the mean deviation from the mean is somewhat greater. However, when the time of transfer is extended to 5 or 6 sec. (data 6) both the mean value and the mean deviation from the mean are increased appreciably. This indicates an uncertain heat loss from the container with increasing delay during transfer. In view of the good agreement between the values for 1 and 3 sec., it follows that negligible heat loss is experienced at the shortest time of transfer, namely, 1 sec. It may also be noted that these data are for an initial temperature of 90° C., when heat loss during transfer should be a maximum.

From data 1, 2, 3, 4, 7, 9, 10, 11 it may be seen that, from each initial temperature, the mean value for the heat capacity of the container, as well as the mean deviation from the mean, is greater when the calorimeter is not evacuated. The differences decrease with lower initial temperatures and practically disappear for an initial temperature of 50° C. The values confirm the appreciable heat loss during transfer in air found with the old calorimeter (2), and vindicate the purpose underlying the design of the new vacuum apparatus. A comparison of data 1 and 5 with 7 and 8 shows rather effectively the advantage of transfers in vacuum as contrasted with similar transfers in air even though the air be dry.

The only unsatisfactory feature of data 1, 2, 3, 4 is the increasing value of the measured heat capacity of the calorimeter with higher initial temperatures. This indicates a small heat loss, probably from radiation, during transit of the container. Providing, however, that the calorimeter is calibrated experimentally, as in the present instance, over the range in which the specific heats of some other substance are to be determined, any error from this source can be eliminated by using the same container and an appropriate weight of the other substance so that the total heat brought down by the container and contents shall be approximately the same as during the calibration.

From the mean deviation from the mean values for the heat capacity of the calorimeter determined with the apparatus evacuated and for a time of transfer of 1 sec., the new calorimeter apparently is capable of an accuracy of certainly better than 0.05%, and probably of about 0.03%.

In view of this precision it would be of interest to redetermine the variation in the specific heat of water with the new calorimeter. The weight of the empty container, however, is too small to give a large enough rise in the temperature of the calorimeter for sufficiently accurate measurement. A mass of about 500 gm. of platinum would be required.

The new calorimeter has been employed for the determination of the specific heats of deuterium oxide over the temperature range 25° to 90° C. This investigation will be the subject of a later paper.

Acknowledgments

References

1. BARNES, W. H. and MAASS, O.   Can. J. Research, 3 : 70-79.   1930.
2. BARNES, W. H. and MAASS, O.   Can. J. Research, 3 : 205-213.   1930.
3. BROWN, R. S., BARNES, W. H., and MAASS, O.   Can. J. Research, 12 : 699-701.   1935.
4. BROWN, R. S., BARNES, W. H., and MAASS, O.   Can. J. Research, B, 13 : 167-169.   1935.
5. INTERNATIONAL CRITICAL TABLES.   McGraw-Hill Book Company, New York.   1929.
6. LANDOLT-BÖRNSTEIN.   Physikalisch-Chemische Tabellen.   Julius Springer, Berlin.   1935.

STUDIES OF CARBON BLACK

V. THE EFFECT OF GAS COMPOSITION ON THE PRODUCTION AND PROPERTIES OF CARBON OBTAINED BY NON-IMPINGEMENT (LAMPBLACK) METHODS[1]

By L. M. PIDGEON[2]

Abstract

Lampblack has been produced from ethylene, propane, methane, and various mixtures of these gases. Carbon liberated from the flame of burning olefines is similar to carbon black in its ability to reinforce rubber, while carbon from paraffins resembles lampblack and does not reinforce rubber. The production of a reinforcing pigment by non-impingement methods is associated with a gas having a negative heat of formation.

Introduction

When a hydrocarbon burns in an adequate supply of secondary air, a luminous flame is produced. The luminosity is due to the presence of particles of carbon, which, being heated to the temperature of the flame gases, radiate in the manner characteristic of incandescent solid bodies. These particles are of minute dimensions and in most cases suffer complete combustion before escaping from the hot zone of the flame. Under suitable conditions, however, notably when the parent gas is a higher hydrocarbon or has a negative heat of formation, some of this carbon may escape from the flame and may be collected by suitable means. Carbon so formed is known as lampblack.

If, on the other hand, the flame impinges upon a relatively cool surface, carbon may be deposited thereon in the form known as carbon black. In practice, the lower members of the paraffin series, such as methane and ethane, are generally employed for this purpose. In the subsequent discussion the terms "impingement" and "non-impingement" will be employed to designate products of the carbon black and the lampblack processes.

While both lampblack and carbon black consist of carbon in a fine state of subdivision, their physical properties are very different. They are readily distinguished by their behaviour when dispersed in vulcanized rubber. Carbon black materially increases ultimate tensile strength and abrasion resistance, and has thereby become the most important reinforcing agent available to rubber technology in all applications where its "colour" is not an objection. Lampblack, on the other hand, does not reinforce rubber and finds restricted uses as a pigment.

While it is generally accepted that the major difference between impingement and non-impingement blacks is one of particle size, it has not been established whether this difference is due to the method of production or to

---

other factors.   Perrot (2) has pointed out that lampblack is normally produced from a complex mixture of hydrocarbons in which the constituents possess large molecules.   These would be expected to yield larger particles than methane and its neighbouring homologues which are normally employed in the carbon black process.   Wiegand (7), on the other hand, differentiates between the two types solely by the method of production, stating that either carbon black or lampblack may be produced from the same gas by choice of suitable methods.

The present work bears directly on this problem.   The production of carbon by non-impingement methods has been carried out using a number of simple hydrocarbons both saturated and unsaturated.   It has been found that the nature of the gas controls to a very considerable extent the properties of the carbon produced by this method.   In general, gases consisting of olefines which have low heats of formation and high heats of combustion yield lampblack which reinforces rubber in a mannner analogous to the action of carbon black.   Paraffins, on the other hand, yield typical lampblack.

It is, therefore, concluded that the particle size of the carbon is related to the heat of formation of the parent gas, paraffins forming large particles, while olefines and acetylene form smaller particles.

A. Production of Lampblack

1. *Apparatus*

The experimental lampblack apparatus as shown in Fig. 1 consisted of a vertical tube in which the gas was burned in a restricted supply of secondary air.   The products of combustion subsequently passed through a filter which removed the carbon escaping from the flame.   The gas issued from a 28% chromium steel tube, which terminated in a $\frac{1}{2}$ in. orifice at C.   The flow of air and gas was metered and controlled with suitable flowmeters, valves, and gasmeters.   In early experiments, difficulty was experienced in producing a smooth flow of secondary air around the flame, and some flickering resulted. This trouble was obviated by the interposition of a number of horizontal sheets of stainless steel gauze D in the path of the air.   With this arrangement a stationary flame could be produced; this is the condition productive of maximum yield.

In later experiments the tube was externally heated, in two sections, the preheat chamber B and the combustion chamber A.   The approximate temperature of the walls of the tube was measured by means of thermocouples which were peaned into small holes drilled in the tube at the centre of each section.

The products of combustion were drawn into the filter E by a suction pump. Additional air was drawn into the chamber at F in sufficient quantity to cool the hot gases.   This expedient allowed the use of a linen filter E backed by a wire gauze.   The accumulated carbon was brushed from the cloth at regular intervals.
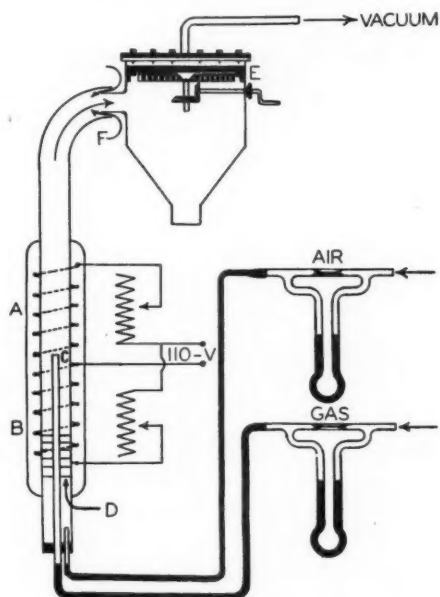
FIG. 1.   *Apparatus.*

2. *Experiments in Unheated Tube*

In these experiments the air necessary to support combustion was drawn in by the natural draft of the vertical tube.   The gas-air ratio was adjusted by altering the size of openings at the base of the tube.   The optimum setting was obtained by trial, and remained constant throughout the experiments described in this section.

Tables I, II, and III show the yields of carbon obtained by partial combustion of various hydrocarbon gases.   By varying the gas rate it was possible, with each gas, to pass through a point of maximum yield.   The theoretical recovery was highest for ethylene and lowest for methane, as would be expected from a consideration of the heats of formation of these gases.

The same gases have been examined in an experimental carbon black apparatus (3, 4) and the following yields obtained:—methane-ethane, 1.3 lb.

TABLE I

PRODUCTION OF CARBON FROM ETHYLENE

Gas rate, cu. ft./min.	Yield, lb./1000 cu. ft.	% Theoretical recovery
0.062	3.3	5.3
0.051	4.4	7.0
0.033	.3.7	5.9

TABLE II

PRODUCTION OF CARBON FROM 85 : 15
METHANE-ETHANE

Gas rate, cu. ft./min.	Yield, lb./1000 cu. ft.	% Theoretical recovery
0.090	1.2	3.3
0.060	1.8	5.0
0.040	1.1	3.0

TABLE III

PRODUCTION OF CARBON FROM 70 : 30
PROPANE-BUTANE

Gas rate, cu. ft./min.	Yield, lb./1000 cu. ft.	% Theoretical recovery
0.075	4.0	3.9
0.060	3.7	3.6
0.043	5.1	4.9
0.031	6.2	6.0
0.027	7.0	6.8
0.013	6.6	6.4

per 1000 cu. ft.; propane-butane, 5.1 lb. per 1000 cu. ft.; ethylene, 4.3 lb. per 1000 cu. ft. If these results are compared with those appearing in Tables I, II, and III, it will be seen that this form of the lampblack apparatus is as efficient as the experimental channel carbon black apparatus.

3. Experiments in Heated Tube

Positive control of the gas-air ratio was possible in the apparatus as shown in Fig. 1. Under normal conditions a flame burning in secondary air in an enclosed space shows signs of stifling if the air supply is less than four times the theoretical requirements for complete combustion to carbon dioxide and water. In the present experiments it was possible to operate with less than the theoretical quantity of air, owing presumably to the fact that the flame temperature was maintained by the auxiliary heating of the tube.

(a) Ethylene—Results of experiments with pure ethylene are shown in Table IV. Optimum yields were obtained at low gas velocities and with an air-gas ratio about 60% of that required for complete combustion. As the air supply was decreased, the temperature in the combustion chamber decreased and more intense auxiliary heat was required to maintain the required temperature. The recovery of 13.3% of the carbon present in the gas is approximately double the maximum obtained in the unheated tube.

(b) Methane-ethane—Of all the gases under consideration, methane has the highest heat of formation and the lowest heat of combustion, and these properties are reflected in the heat requirements and carbon yields. As seen

TABLE IV

PRODUCTION OF CARBON FROM ETHYLENE

(Theoretical air-gas ratio for complete combustion is 15 : 1)

Gas, cu. ft./min.	Air, cu. ft./min.	Air : gas	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.03	0.25	8.3 : 1	1100	550	6.7	10.8
.03	.33	11.0 : 1	1100	550	7.0	11.2
.03	.40	13.3 : 1	1100	550	6.8	10.9
.02	.40	20.0 : 1	1000	550	7.5	12.0
.02	.30	15.0 : 1	1000	550	7.4	11.9
.02	.25	12.5 : 1	1000	550	8.3	13.3
.02	.18	9.0 : 1	1000	700	8.3	13.3
.02	.12	6.0 : 1	1000	700	7.3	11.7

in Table V the maximum yield was obtained with the theoretical air-gas ratio, any reduction in air supply resulting in lower yields.

With this gas the carbon recovery is 2.5 to 3 times that obtained by the channel process.

(c) Propane-butane—Results of experiments with this gas mixture are shown in Table VI. In this case, maximum recovery was obtained with less air than that required for complete combustion. Much less auxiliary heat was required than with methane, as would be expected from the higher heat of combustion of propane and butane. Yields were generally double those obtained in the unheated tube or in the channel apparatus.

(d) Synthetic mixture of ethylene (33%), methane-ethane (50%), and hydrogen (17%)—While pure ethylene is unlikely to be available in commercial quantities for the production of carbon black, mixtures of this gas with hydrogen and other paraffins are readily obtained by the pyrolysis of propane-butane, and similar gases. Experiments have already been described (4) in which gases produced in this manner have been utilized for the production of carbon black in an experimental plant of the channel type. It will be shown in the succeeding section that the lampblack produced from ethylene has

TABLE V

PRODUCTION OF CARBON FROM 85 : 15 METHANE-ETHANE

(Theoretical air-gas ratio for complete combustion approx. 10 : 1)

Gas, cu. ft./min.	Air, cu. ft./min.	Air : gas	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.02	0.20	10 : 1	1000	700	3.9	10.8
.02	.16	8 : 1	1000	700	2.5	6.9
.02	.12	6 : 1	1000	700	2.1	5.8

TABLE VI

PRODUCTION OF CARBON FROM 70 : 30 PROPANE-BUTANE

(Theoretical air-gas ratio for complete combustion is 25 : 1)

Gas, cu. ft./min.	Air, cu. ft./min.	Air : gas	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.02	0.50	25.0 : 1	1100	400	12.8	12.4
.02	.30	15.0 : 1	1000	550	13.0	12.6
.02	.15	7.5 : 1	1000	700	7.4	7.2

properties very similar to those of carbon black, and it therefore was interesting to ascertain the extent to which these properties would be maintained when an appreciable portion of the ethylene was replaced by other gases.

In Table VII the results of experiments on a synthetic gas are shown. In this gas an ethylene content of 33% replaces 25% ethylene, 3 to 4% propylene, and 1% acetylene contents, all of which occurred in these proportions in the pyrolysis off-gas referred to previously. The additional 8% ethylene was regarded as equivalent to the propylene-acetylene mixture in its ability to produce carbon. The carbon recovery based on the theoretical was 17% higher than any obtained previously.

TABLE VII

PRODUCTION OF CARBON FROM C_2H_4 33%, H_2 17%, CH_4 50%

Gas, cu. ft./min.	Air, cu. ft./min.	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.02	0.20	1000	700	5.6	15.6
.02	.20	1000	700	5.4	15.1
.02	.20	1000	700	5.4	15.1

B. Reinforcement of Rubber by Lampblack

While the physical properties of finely divided carbon may be evaluated in several ways, its behaviour in rubber has the greatest practical interest. Rubber tests have been carried out using the following formula: smoked sheet, 100; zinc oxide, 3; stearic acid, 2; sulphur, 5; diphenylguanidine, 0.75; carbon, 35 parts. Mixes were made on a laboratory roller mill and they were then vulcanized on a four-cavity mold in a steam press at 141.5° C. for various times as shown in the tables. Tensile tests were carried out with dumb-bell test pieces. Samples of standard channel blacks and lampblacks were examined simultaneously; hence curing and testing conditions were identical in any given group. Hardness was measured by means of the "Shore durometer".

Owing to the relatively low yields of carbon that are obtainable by means of all flame methods, it was not possible in every case to obtain sufficient carbon black to conduct full-scale rubber tests. The values appearing in Table VIII were obtained with a rubber mix of one-half the usual weight (281.5 gm.) employed in these experiments, and are in all cases lower than usual. The values in Table IX are more normal in this respect. Despite some discrepancies the results show clearly that the composition of the parent gas affects the physical properties of lampblack as exhibited in rubber.

TABLE VIII

TENSILE PROPERTIES OF RUBBER

Cure, min.	Modulus at elongation of					T_B	E_B	Hardness
	200%	300%	400%	500%	600%			
"F"								
65	34.0	62.0	106	146	217	227	620	55
85	43.5	85.0	131	189	256	256	600	55
105	43.8	86.0	131	185	245	249	600	58
"E" (produced from ethylene in unheated tube)								
65	55.6	88.5	138	220	262	262	600	60
85	52.3	74.6	132	206	270	270	600	60
105	40.5	77.0	130	192	252	272	620	57
Lampblack (Lumersheim)								
65	79.0	119.5	150	180	—	185	520	50
85	53.5	90.7	132	190	—	193	505	53
Cabot's "Spheron" (Channel black)								
65	40.0	63.5	125	184	—	242	560	53
85	39.0	76.5	128	186	248	264	630	55
105	45.0	86.0	144	206	—	267	600	53

In Fig. 2 the stress-strain curves at optimum cure are shown for carbons produced from various gases. The ethylene sample is almost identical with the channel black. The propane-butane sample, on the other hand, resembles a typical "soft" or "thermatomic" carbon producing a reasonably high ultimate tensile strength but exerting little stiffening. The commercial lampblack shows no reinforcement, so that the resultant product, while it is stiff, breaks short at low tensile values.

The carbons produced from olefines and paraffins in the heated tube showed less difference than those obtained in the unheated, but the superior reinforcement given by the carbon produced from the unsaturated gas was still very obvious.
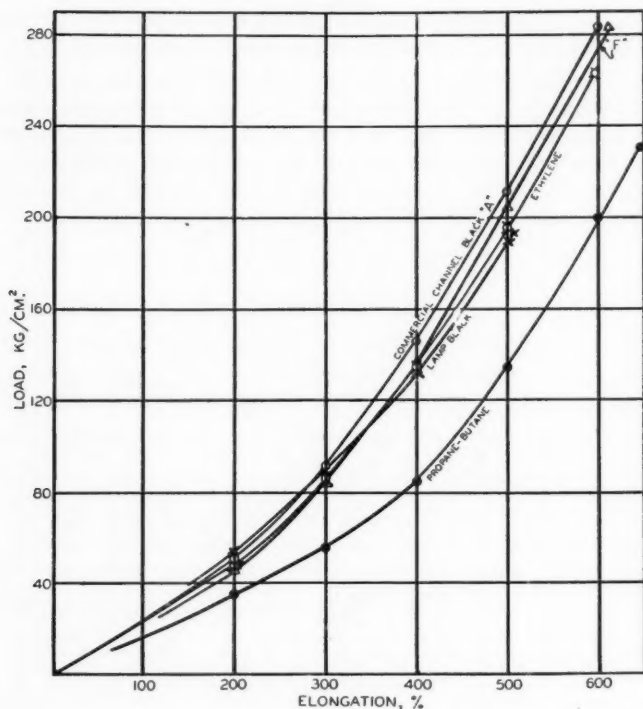
FIG. 2.   *Reinforcement of rubber.*

Sample *F* was obtained from the upper portions and flues of the experimental channel carbon black apparatus described previously (4). When the apparatus was operated with gases rich in olefines the flames were very "smoky", and appreciable amounts of carbon escaped from the channels, a portion of which remained in the flues. It is generally considered that the carbon which escapes from the channels does not exhibit the properties of carbon black, and this is undoubtedly the case when the gas undergoing combustion consists of paraffins (5). When olefines are present, however, the properties of the resultant black resemble those of carbon black, as seen in Tables VIII, IX, and Fig. 2. In the case of a channel plant operating on olefine-bearing gases, it would be desirable to collect, if possible, the carbon escaping from the channels. If this procedure had been adopted in the experiments described previously (4), the yields obtained from pyrolysis waste gases would have been considerably improved.

The properties of carbon produced from synthetic gas of approximately the same content of olefines as the pyrolysis waste gases examined previously are only slightly inferior to those of carbon produced from pure ethylene, as shown in Table X.

TABLE IX

TENSILE PROPERTIES OF RUBBER

Cure, min.	Modulus at elongation of					T_B	E_B	Hardness
	200%	300%	400%	500%	600%			
N5 Propane-butane (Unheated tube)								
65	31.9	50.8	74.0	109	162	194	650	—
85	33.2	54.5	83.4	138	192	211	633	57
105	35.1	56.5	84.8	134	200	230	645	58
125	33.9	54.2	82.2	129	182	218	647	51
N13 Ethylene (Unheated tube)								
65	40.5	69.0	108	166	229	250	627	57
85	48.6	81.3	126	184	252	253	602	59
105	48.0	86.0	134	196	259	263	595	60
125	46.9	83.4	129	186	234	230	576	58
Cabot's "Spheron"								
65	37.3	66.3	108	169	227	267	653	57
85	41.5	77.1	124	193	264	289	630	58
105	50.8	92.5	146	212	284	284	595	60
125	54.4	94.8	153	215	287	284	596	63
"F"								
65	38.8	58.5	112	169	237	241	605	57
85	42.0	77.7	129	188	265	265	600	60
105	46.4	85.1	136	204	275	283	608	63
125	50.0	88.3	142	209	—	276	590	64

Conclusions

The reinforcement of rubber is probably a sorption process, this term being used in its widest possible sense. The magnitude of reinforcement will therefore depend on the bond existing between the carbon particle and the rubber molecule and on the size of the particle. Owing to the difficulty of measuring the former factor and to ignorance as to its real nature, it is convenient to consider that differences in reinforcement of rubber are due solely to difference in particle size, it being realized at the same time that this cannot be the only important factor. The particle size of lampblacks and thermatomic blacks is much larger than that of carbon blacks. This is indicated by oil adsorption, and by the opacity of dilute suspensions of known concentration. If, then, carbon black, which reinforces rubber, consists of fine particles, it may be concluded that the carbon which escapes from an ethylene flame has a much smaller particle size than that which escapes from a paraffin flame. This assumption seems to be readily reconcilable with the thermochemical properties of the gases.

TABLE X

TENSILE PROPERTIES OF RUBBER

Cure, min.	Modulus at elongation of					T_B	E_B	Hardness
	200%	300%	400%	500%	600%			
Ethylene (Heated tube)								
65	26.6	51.0	80.0	125	182	235	670	50
85	33.6	57.5	90.3	141	210	260	660	54
105	34.7	59.0	88.0	140	210	262	660	52
125	33.6	60.0	91.8	148	209	246	660	53
Propane-butane (Heated tube)								
65	20.0	35.8	54.0	81.5	132	153	620	42
85	24.4	43.0	63.0	102	155	187	640	45
105	25.7	43.1	70.0	104	175	218	650	47
125	29.2	50.0	76.0	125	186	228	670	50
Ethylene, Methane, Hydrogen (Heated tube)								
65	24.4	43.0	71.5	111	176	212.2	650	47
85	30.0	53.5	85.0	142	205	254	660	48
105	35.8	62.5	97.0	161	225	247	610	51
125	35.8	63.5	97.5	160	232	252	620	53
Cabot's "Spheron"								
65	28.2	56.5	96.5	153	217	235	625	55
85	38.7	75.0	118	185	256	272	620	55
105	39.8	79.8	127	199	273	276	605	61
125	49.1	88.5	146	215	—	280	585	61

The dissociation of ethylene is exothermic to the extent of some 4000 cal. per mole. Ethylene dissociates readily in the gas phase since the required energy is already resident in the molecule and does not have to be supplied by radiation or conduction from hot zones outside the "cracking" region. Thus the reaction is largely homogeneous and a large number of small particles are formed which do not increase in size because, after their formation, the reaction is complete.

Paraffins, on the other hand, must be supplied with heat in order to cause dissociation, methane, the most stable paraffin, requiring some 21,000 cal. per mole. It is difficult to supply heat to gases as they are transparent to radiation and poor conductors of heat. Methane will not decompose in the gas phase at reasonable velocities until temperatures higher than 1200 ° C. are attained (6). At these temperatures the heterogeneous reaction is rapid. When a particle is formed by the dissociation of an activated hydrocarbon molecule it becomes a nucleus which is a good radiation absorber and will be maintained at a high temperature, thereby providing a surface upon which further heterogeneous reaction will take place. Thus as long as the particle remains in the heated zone it will grow in size.

In the channel process this agglomeration is arrested by the relatively cool plate, which collects a fraction of the particles before they have time to grow. In the lampblack process the particles have much longer time to aggregate, but, as we have seen, if the decomposition of the hydrocarbon is an exothermic reaction, the tendency is not greater than in the channel process.

If these conclusions are carried a step further, it seems clear that the addition of acetylene to paraffins would produce even finer particle sizes. It is possible that a suitable combination of acetylene and paraffin might produce by lampblack methods a carbon with properties identical with those of carbon black. The advantages of the process would be higher yields and the utilization of more compact apparatus. Large flames could be employed and the channel plant, with its enormous complication of piping and small burner tips and its high initial cost and corrosion problems, would be eliminated.

References

1. GEHMAN, S. D. and MORRIS, T. C. Ind. Eng. Chem., Anal. ed. 4 : 157-162. 1932.
2. PERROTT, G. ST. J. U.S. Bur. Mines Bull. 192. 1922.
3. PIDGEON, L. M. Can. J. Research, B, 14 : 127-137. 1936.
4. PIDGEON, L. M. Can. J. Research, B, 15 : 139-155. 1937.
5. PLUMMER, W. B. and KELLER, T. P. Ind. Eng. Chem. 22 : 1209-1211. 1930.
6. STANLEY, H. M. and NASH, A. W. J. Soc. Chem. Ind. 48 : 1-8T. 1929.
7. WIEGAND, H. B. Ind. Eng. Chem. 23 : 178-181. 1931.

SELENIUM IN CANADA[1]

By Horace G. Byers[2] and H. W. Lakin[3]

Abstract

The existence of an enormous area of seleniferous soil is revealed through the results of a reconnaissance examination of portions of Alberta, Saskatchewan, and Manitoba provinces of Canada. About 300 samples of shales, soils, and plants were collected at 90 different locations. The selenium content of the shales varied from 0.3 to 3.0 p.p.m., and of the soils from 0.1 to 6 p.p.m. The vegetation contained from 3 to 4190 p.p.m. of selenium.

The investigations which have been carried out in the Department of Agriculture on the occurrence and distribution of selenium in soils have led far afield (3, 4, 5, 8), and have demonstrated, among other things, a close correlation between the geological strata from which soils have developed and the quantity of selenium found in the soils. Following up various indications, it has been shown that selenium in quantities sufficient to render some, though not all, forms of vegetation toxic is likely to be present in soils derived from Cretaceous shales. Areas of greater or less magnitude and of varied intensity of toxicity have been found in all the states where such soils occur, so far as they have been investigated. Among the areas examined one of the largest is the northern tier of counties of Montana (4, 8). The geological formations responsible for these soils include not only certain Cretaceous sediments but also pre- and post-Cretaceous formations (1, 2).

Geological formations of the same type cover enormous areas in the provinces of Alberta and Saskatchewan in Canada. At the suggestion of Dr. L. E. Kirk of Saskatchewan University, a reconnaissance examination of these areas was made in the spring of 1938. During a considerable portion of the examination the writers were accompanied by J. L. Bolton, of the Dominion Agricultural Experiment Station at Swift Current, who carried out the botanical identifications given in the text.

In the course of the investigations it has become very clear that certain plants may be used as "indicators" of seleniferous areas since they are certain to contain selenium if any is present in available form. Among these plants, known to occur under the soil and climatic conditions in west central Canada, are two species of Astragalus (A. pectinatus and A. bisulcatus). The examination of the area was therefore so timed that these plants would be in bloom and readily observed. In all, about 300 samples of shales, soils, and plants were collected at 90 different locations. These locations were selected, for the most part, because of the occurrence of the plants mentioned. In a few instances associated plants were included. The locations from which the

samples were taken may readily be ascertained by means of automobile road maps of the area. No attempt will be made here to detail the data obtained. These data will be presented in a Department publication. The results may be summarized as follows:

The Geological maps of the Canadian Bureau of Mines, Nos. 204A and 267A, show extensive exposures of geological formations of the Cretaceous period which are identified under the names St. Mary's River, Fox Hills, Bearpaw, Belly River, Pakowki, and Milk River on the Calgary sheet (No 204A) in eastern Alberta and western Saskatchewan. These correspond in a general way with the Fox Hills, Bearpaw, Judith River, Claggett, Eagle, and Telegraph formations of Montana and to the various subdivisions of the Pierre formation in South Dakota and Nebraska (4, 6). No extensive outcrops of older Cretaceous formations corresponding to the Niobrara and other members of the Colorado shales are mapped.

Still larger areas of these shales are exposed formations shown on the Regina sheet (No. 267A) over the whole southern portion of Saskatchewan. Of these the most widespread are the Bearpaw and Belly River formations. Over considerable portions of both southern Alberta and Saskatchewan the actual soils rest upon post-Cretaceous formations which form irregular "islands" on the maps. Geological identification of the underlying strata in part of the area has not been published. A considerable portion of the area examined is covered by soils derived from Glacial Drift.

Of these shale formations about 50 samples were collected at 24 locations. All the samples on examination were found to contain selenium in quantities ranging from 0.3 to 3.0 p.p.m. In none of the concretions examined were there noted any showing concentration of selenium. In some instances astragalus plants were found growing in the shales. Notable among such cases is one at a point three miles north of Swift Current, Saskatchewan, where Bearpaw shale containing 1.5 p.p.m. of selenium supported an *Astragalus pectinatus* plant containing 3360 p.p.m. of selenium. Since vegetation containing more than 3 p.p.m. of selenium (7) may be regarded as somewhat injurious, this sample is to be regarded as intensely toxic.

Another sample of a fissile shale (presumably Judith River), 109 miles north of Swift Current on Route 4, contained 1 p.p.m. of selenium while the air-dry sample of *A. pectinatus* growing on this shale contained 2440 p.p.m. By contrast, a sample of shale $4\frac{1}{2}$ miles northwest of Bow Island, Alberta (presumably Belly River formation), contained 0.5 p.p.m. of selenium, and *A. bisulcatus* growing in it had but 25 p.p.m.

Soil samples were taken at 80 locations. While usually these were only surface samples, in a few cases profiles were taken. All the soil samples were immediately under at least one of the plant specimens. The quantities of selenium found in the soil samples ranged from 0.1 to 6 p.p.m. and only at 25 locations did the concentration of the surface soil reach or exceed 1 p.p.m. The general character of the soils and the quantity of selenium found are similar to the conditions noted in northern Montana (8).

The purpose of the examination being simply a reconnaissance, no attempt was made to determine the degree of toxicity of food and forage plants. The indicator plants of the *Astragalus* family were used as a guide in selecting locations; and in general where neither *A. pectinatus* nor *A. bisulcatus* occurred, no samples were taken. Where these plants were found in abundance, occasionally other plants were selected, partly in the hope of finding other indicator plants. In all, about 100 plant samples were collected. The analyses of these plants are listed in Table I.

TABLE I

SELENIUM CONTENT OF ASTRAGALI SAMPLES FROM ALBERTA, SASKATCHEWAN, AND MANITOBA, CANADA

Lab. No.	Field No.	Location	Material	Selenium content, p.p.m.
Alberta				
B23069	17A	47 mi. W. of Maple Creek, 1 mi. W. of Pashley	*A. pectinatus*	640
B23070	18A	52 mi. W. of Maple Creek, 6 mi. W. of Pashley	*Poa secunda* (grass)	10
B23072	19A	5 mi. SW. of Medicine Hat, Route 3	*A. bisulcatus*	240
B23074	20A	16 mi. SW. of Medicine Hat, Route 3	*A. pectinatus*	3690
B23075	20B	16 mi. SW. of Medicine Hat, Route 3	Winter rye (immature heads)	8
B23077	21A	½ mi. E. of Bow Island, Route 3	*A. pectinatus*	3520
B23378	21B	½ mi. E. of Bow Island, Route 3	Young wheat (4 to 5 in.)	80
B23080	22XA	4½ mi. NW. of Bow Island on road to Ferry	*A. bisulcatus*	25
B23082	22YA	4½ mi. NW. of Bow Island on road to Ferry	*Dondia intermedia*	3
B23084	22ZA	4½ mi. NW. of Bow Island on road to Ferry	*A. bisulcatus*	30
B23086	23A	15 mi. W. of Bow Island on Route 3	*A. pectinatus*	370
B23088	24A	36 mi. W. of Bow, Route 3	*A. pectinatus*	1680
B23090	25A	1 mi. W. of Lethbridge	*A. bisulcatus*	470
B23098	26ZA	6 mi. NE. of Milk River	*A. pectinatus*	670
B23104	28A	12 mi. E. of Milk River (Verdigris Coulee)	*A. pectinatus*	340
B23118	30A	½ mi. N. of Coutts on Route 4	*A. pectinatus*	190
B23120	31A	4 mi. N. of Coutts on Route 4	*A. pectinatus*	280
B23122	32A	10 mi. N. of Coutts on Route 4	*A. pectinatus*	140
B23124	33A	32 mi. N. of Coutts on Route 4	*A. pectinatus*	150
B23126	34A	46 mi. NW. of Coutts on Route 4	*Thalaspi arvense* (stinkweed)	12
B23127	34B	46 mi. NW. of Coutts on Route 4	*Sisymbrium altissimum*	35
B23128	34C	46 mi. NW. of Coutts on Route 4	*A. pectinatus*	700
B23133	36A	93 mi. SE. of Calgary on Route 23	*A. pectinatus*	1260
B23135	37A	82 mi. SE. of Calgary on Route 23	*A. pectinatus*	460
B23140A	39A	1½ mi. E. of Morley	*A. succulentum*	25
B23146	42A	5 mi. W. of Calgary on Route 1	*A. pectinatus*	730
B23148	43A	20 mi. E. of Calgary on Route 9	*A. pectinatus*	1130
B23150	44A	20 mi. W. of Drumheller on Route 9	*A. bisulcatus*	60
B23152	45A	3 mi. N. of Drumheller on Route 9	*A. bisulcatus*	140
B23155	46A	Lake Sullivan, 13 mi. SE. of Halkirk	*A. bisulcatus*	12
B23156	46B	Lake Sullivan, 13 mi. SE. of Halkirk	*A. goniatus*	25
B23157	46C	Lake Sullivan, 13 mi. SE. of Halkirk	*Homalobus tennellus* (Rydberg)	80
B23158	46D	Lake Sullivan, 13 mi. SE. of Halkirk	A. hay (mixed 46A, B, C) (3 years old)	20
B23160	47A	13 mi. SE. of Brooks on Route 2	*A. pectinatus*	1390
B23162	48A	36 mi. SE. of Brooks on Route 2	*A. pectinatus*	190
B23163	48B	36 mi. SE. of Brooks on Route 2	*Cheirinia inconspicua* (mustard)	10
B23164	48C	36 mi. SE. of Brooks on Route 2	*Pentstemon albidus*	60
B23166	49A	Medicine Hat on Route 2	*A. bisulcatus*	100
B23167	49B	Medicine Hat on Route 2	*Sideranthus grindelioides* (Rydberg)	10

TABLE I—*Continued*

SELENIUM CONTENT OF ASTRAGALI SAMPLES FROM ALBERTA, SASKATCHEWAN, AND MANITOBA, CANADA—*Continued*

Lab. No.	Field No.	Location	Material	Selenium content, p.p.m.
Alberta— conc.				
B23169	50A	5 mi. F. of Medicine Hat on Route 2	*A. pectinatus*	610
B23170	50B	5 mi. E. of Medicine Hat on Route 2	*Cheirinia aspera* (Prairie Rocket)	15
Saskatchewan				
B23025	5A	10 mi. S. of Outlook on Route 45	*A. pectinatus*	1000
B23027	6A	10 mi. W. of Elbow	*A. bisulcatus*	15
B23028	6B	10 mi. W. of Elbow	*A. missouriensis*	5
B23029	6C	10 mi. W. of Elbow	*Oxytropis gracilis*	4
B23030	6D	10 mi. W. of Elbow	*Chamaerhodos nuttalli*	20
B23031	6E	10 mi. W. of Elbow	*Astragalus* sp?	10
B23037	8A	4 mi. E. of Elbow	Yellow compositae	15
B23038	8B	4 mi. E. of Elbow	*A. pectinatus*	4060
B23039	8C	4 mi. E. of Elbow	*Aplopappus spinulosus*	260
B23041	9A	2 mi. S. of Herbert on Route 1	*A. pectinatus*	1150
B23044	11A	6 mi. W. of Cadillac	*A. bisulcatus*	1020
B23045	11B	6 mi. W. of Cadillac	*Hymenoxys Richardsonii* (Colorado rubber plant)	20
B23049	12A	4 mi. NE. of Eastend at exposure of Eastend formation.	*A. pectinatus*	1210
B23059	14A	9 mi. SW. of Eastend on Route 13	*A pectinatus*	160
B23064	15A	10 mi. S. of Maple Creek on Route 21	*A. bisulcatus*	50
B23065	15B	10 mi. S. of Maple Creek on Route 21	*Poa canbyi* (Scribn. Piper) "Canby bluegrass"	8
B23067	16A	12 mi. NW. of Maple Creek on Route 1	*A. pectinatus*	160
B23172	51A	13 mi. E. of Maple Creek on Route 1	*A. pectinatus*	2310
B23174	52A	60 mi. E. of Maple Creek on Route 1	*A. pectinatus*	790
B23015	1A	3 mi. N. of Swift Current on Route 4	*A. pectinatus*	3360
B23017	2A	24 mi. N. of Swift Current	*A. bisulcatus*	1150
B23176	53A	30 mi. N. of Swift Current on Route 4	*A. bisulcatus*	490
B23178	54A	35 mi. N. of Swift Current on Route 4	*A. bisulcatus*	340
B23180	56A	66 mi. N. of Swift Current on Route 4	*A. pectinatus*	120
B23180A	56C	66 mi. N. of Swift Current on Route 4	Large mushroom	10
B23019	3A	103 mi. N. of Swift Current on Route 4	*A. bisulcatus*	3640
B23021	4A	109 mi. N. of Swift Current on Route 4	*A. pectinatus*	2440
B23181	57A	7 mi. N. of Rosetown on Route 4	Young *A. bisulcatus* (on glacial drift)	3240
B23183	58A	3 mi. E. of Biggar on Route 14	*A. pectinatus*	220
B23185	59A	University campus, Saskatoon	*A. pectinatus*	1540
B23187	60A	13 mi. E. of Saskatoon on Route 14	*A. pectinatus*	780
B23188	60B	13 mi. E. of Saskatoon on Route 14	Young spring wheat	30
B23191	61A	64 mi. E. of Saskatoon on Route 14	*A. pectinatus*	1100
B23193	62A	164 mi. E. of Saskatoon on Route 14	*A. bisulcatus*	500
B23195	63A	3 mi. SE. of Kamsack on Route 8	*A. bisulcatus*	640
B23197	64A	3 mi. SE. of Kamsack on Route 8	Dandelions	110
B23200	65A	2½ mi. SE. of Kamsack on Route 8	*Hedysarum* sp?	60
B23202	66A	2½ mi. SE. of Kamsack	*A. bisulcatus*	350
B23208	68A	56 mi. SE. of Yorkton on Route 14	*A. bisulcatus*	320
B23223	77A	18.7 mi. N. of Burrows on road to Esterhazy	*A. bisulcatus*	420
B23226	79A	1 mi. W. of Broadview on Route 1	*A. pectinatus*	4190
B23227	79B	1 mi. W. of Broadview on Route 1	Western wheat grass	35
B23228	79C	1 mi. W. of Broadview on Route 1, 50 feet from 79.	*A. bisulcatus*	1020
B23276	80A	23 mi. W. of Grenfell on Route 1	*A. pectinatus*	1040
B23278	81A	61 mi. W. of Grenfell on Route 1	*A. pectinatus*	2590

TABLE I—*Concluded*

SELENIUM CONTENT OF ASTRAGALI SAMPLES FROM ALBERTA, SASKATCHEWAN, AND MANITOBA, CANADA—*Concluded*

Lab. No.	Field No.	Location	Material	Selenium content, p.p.m.
Saskatche-wan— conc.				
B23280	82A	13 mi. S. of Regina on Route 6	Young wheat, 4 in.	120
B23282	83A	36 mi. SE. of Regina on Route 39	A. bisulcatus	1950
B23283	83B	36 mi. SE. of Regina on Route 39	Young wheat	140
B23285	84A	57 mi. SE. of Regina on Route 39	A. pectinatus	2370
B23287	85A	1 mi. SE. of Weyburn on bank of Souris River on Route 39	A. bisulcatus	2130
B23289	86A	22 mi. SE. of Weyburn on Route 39	A. pectinatus	650
B23291	87A	31 mi. SE. of Weyburn on Route 39	A. bisulcatus	830
B23292	87B	31 mi SE. of Weyburn on Route 39	Lambsquarters (*Chenopodium* sp?)	45
B23296	89A	13 mi. SE. of Estevan on Route 39	A. pectinatus (seeds)	2530
B23298	90A	24 mi. SE. of Estevan on Route 39	A. pectinatus	1050
Manitoba				
B23210	69A	½ mi. E. of Saskatoon-Manitoba line on Route 4	A. bisulcatus	330
B23213	71A	2 mi. E. of Saskatoon-Manitoba line on Route 4	A. bisulcatus	420
B23215	72A	17 mi. SE. of Russell on Route 4	A. bisulcatus	880
B23217	73A	5 mi. SW. of Mineota, base of bluffs of Assiniboine	A. bisulcatus	160
B23219	74A	4 mi. W. of Elkhorn on Route 1	A. bisulcatus	890

Consideration of the data in Table I leads to a number of definite observations, especially when account is taken of previously obtained information and of the geological and geographical maps of the area.

Definitely, toxic vegetation is produced on soils derived from Cretaceous shales over very considerable areas in Alberta, larger areas in Saskatchewan, and a much smaller area in Manitoba. No estimate is offered concerning the number of square miles involved. Such estimate is not only impossible because of the limited scope of the investigation but because no attempt was made to sample areas not shown as Cretaceous, and when of Cretaceous origin, only if external indications of the presence of selenium were observed.

The samples of *A. pectinatus* (narrow leaf milk vetch) and of *A. bisulcatus* (two-grooved milk vetch) show the same variation of selenium content which has been observed elsewhere, and may be considered as indicating a wide variation in intensity of toxicity of the soils. In no case is selenium absent, the range being from 15 to 4190 p.p.m. None of the small number of other plants collected proves to be a selenium indicator except possibly *Homalobus tennellus*, 46C (*A. Tennellus* (Gray)), and *Chamaerhodos nuttalli*, 6D.

The samples of young wheat, 21B, 60B, 82A, and 83B, indicate the distinct possibility of toxic vegetation of the ordinary food or forage types. The sample 82A is especially interesting because it is from an area in which cursory investigation revealed no specimens of Astragali but the soil itself is very similar

to seleniferous soils found in the United States. The quantities of selenium found in samples 15B, 18A, 20B, 34B, 48B, 48C, 64A, 79B, and 87B, also point clearly to the presence of moderately toxic areas of farm and ranch land and the probability of toxic food in certain areas.

One of the most interesting observations made was that in the section about Lake Sullivan, Alberta, hay, consisting in large part of *A. bisulcatus*, was used for feed during periods of feed shortage due to drought. One of these cases was investigated. The farmer in question reported that very little of this hay was actually eaten and that it was offered to the animals but once a week. His observation was that horses refused it absolutely and cattle and sheep ate it very sparingly. He considered this to be due to the presence of unpalatable fox tail which formed a large part of the hay. Since the animals refused the hay it was disposed of by use as thatch for the stables. The green plants in question and the three-year-old dry hay gave the results shown for numbers 46A, 46B, 46C, and 46D. It is clear that this material is unfit for forage and was so recognized by the animals themselves.

The data obtained point to the following:

While the existence of an enormous area of seleniferous soil is revealed and while definite evidence of injury is apparent, it does not follow that it presents a sufficiently serious situation to warrant any drastic remedial procedures except as further investigation of local areas may indicate. The evidence, taken together with previously assembled data, indicates very decidedly that overgrazing of the affected lands may produce serious injury through consumption by hungry animals of toxic plants not normally eaten by animals. It seems probable that within seriously toxic limited areas human injury may be produced when the total diet is composed of locally grown foods.

Supplementary observation and local information point to considerable injury to, and loss of stock through, troubles known locally as "frozen feet." One of the characteristics of selenium poisoning is malformation and even loss of hoofs of livestock, which effects can well be mistaken as due to freezing. How extensive this loss and how fully due to selenium poisoning may be ascertained only by detailed study of the areas.

The most important observation, aside from the extension of the area of seleniferous soils of toxic type, lies in the fact that glacial soils may be toxic. This fact points to a needed widening of the field of study in the United States.

References

1. BEATH, O. A., EPPSON, H. F., and GILBERT, C. S.   Univ. Wyo. Agr. Expt. Sta. Bull. 206. 1935.
2. BEATH, O. A., GILBERT, C. S., and EPPSON, H. F.   Am. J. Botany, 24 : 96-101.   1937.
3. BYERS, H. G.   U.S. Dept. Agr. Tech. Bull. 482.   1935.
4. BYERS, H. G.   U.S. Dept. Agr. Tech. Bull. 530.   1936.
5. BYERS, H. G., MILLER, J. T., WILLIAMS, K. T., and LAKIN, H. W.   U.S. Dept. Agr. Tech. Bull. 601.   1938.
6. MOXON, A. L.   South Dakota Agr. Expt. Sta. Bull. 311.   1937.
7. MUNSELL, H. E., DeVANEY, G., and KENNEDY, M. H.   U.S. Dept. Agr. Tech. Bull. 534. 1936.
8. WILLIAMS, K. T., LAKIN, H. W., and BYERS, H. G.   U.S. Dept. Agr. Tech. Bull.   In press.